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BUREAU OF STANDARDS JOURNAL OF RESEARCH

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AN IMPROVED FORM OF STANDARD IONIZATION CHAMBER [1]

By Lauriston S. Taylor and George Singer

ABSTRACT

modification of the open-air parallel plate ionization chamber, readily port- and adapted to field use, is described. In this chamber, narrow guard plates supplemented by a system of 10 guard wires across the ends of the chamber. wires are so spaced that X-ray scattering from them is negligible. By this ns a uniform electrostatic field between electrodes is obtained without the of wide guard plates and the large plate-to-shield spacing necessary in the mary standard. This design has permitted a decrease in the volume and ght of the secondary standard by a factor of 15.

The results of direct comparisons between this chamber and the primary ndard are given and indicate that the Roentgen can be reproduced by the mer with the same accuracy as the primary standard. The problem of dia- agming is identical for the two chambers, and for a given tube the same erse power law holds for both. Like the standard chamber, the new chamber s not require that corrections be made for differences in X-ray quality.

Any of the usual electrostatic measuring systems may be used with this chamber hough for precise work a null or current compensation system is desirable.

It is expected that this type of chamber will be found useful in the international nparisons of the Roentgen now pending, for which purpose the "fingerhut- mmer" is generally inadequate.

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I. INTRODUCTION

The unit of intensity of an X-ray beam has been defined [2] in rms of the ionization produced in 1 cubic centimeter of unrestricted mospheric air [3]; and as a result the air ionization chamber is, at st temporarily, established as the primary standard for X-ray tensity measurements.

Two distinct types of standard ionization chambers have been ed; (*a*) The pressure air chamber, designed by Thaller [4] and by hnken [5, 6] to give comparatively large ionization currents, meas-

[1] Paper read before Radiological Society of North America, Toronto meeting, December 2 to 6, 1929.
[2] Second International Congress of Radiology, Stockholm; July 23 to 27, 1928.
[3] Paragraphs 2 and 3. "Report of International X-Ray Unit Committee" (Recommended) "2. That e International Unit be the quantity of X-radiation which when the secondary electrons are fully utilized d the wall effect of the chamber is avoided, produces in 1 cubic centimeter of atmospheric air at 0° C. and cm. mercury pressure such a degree of conductivity that one electrostatic unit of charge is measured at uration current." (Recommended.) "3. That the International Unit of X-radiation be called the ntgen' and that it be designated by the small letter *r*."
[4] R. Thaller, O. Berg. and W. Schwerdfeger, Wissenschaftliche Veroffentlichungen aus dem Siemenskon- rn, 3, p. 162; 1924.
[5] H. Behnken, Zeit. fur Techn. Phys., **5**, p. 3; 1924.
[6] H. Behnken, Zeit. fur Techn. Phys., **2**, p. 563, 1926.

urable without the use of extremely sensitive instruments; (*b*) T atmospheric pressure air chamber, of which the construction a manipulation is comparatively simple. The first type was employe by the Physikalisch-Technischen-Reichsanstalt until their re recent adoption of a cylindrical form of atmospheric air chamb In this country the second type has been used exclusively.

The atmospheric or open-air chamber was conceived as a result Villard's definition of the "*e*" unit in 1908,[7] and was later develope by Friedrich.[8] As a result of further refinements by Duane,[9] Glasser Failla,[11] Kustner,[12, 13] the authors,[14, 15] and others, it is now apparent adequate for present demands. Using well-controlled, constant vol age on the X-ray tube, correct diaphragming of the X-ray beam a a refined measuring technique, the Roentgen can be reproduced the present time at the National Bureau of Standards with a mea deviation of about ±0.5 per cent.[16]

It is not sufficient, however, that the unit be duplicable in any o laboratory, but there must be also good agreement between the uni as determined by all standardization laboratories. In the establis ment of standards, it is obviously desirable to have them correct one significant figure better than the magnitudes they are used certify. Applied in the case of the international Roentgen uni medical practice demands an accuracy of 5 per cent in the calibrati of its ionometers, the national standardization centers should bri about an agreement, if possible, between their respective standar of 0.5 per cent. There has been as yet, however, no direct check the Roentgen between the national standardizing laboratories.

The only comparison of international character was made b Behnken [17] in 1927 before a standard was developed at the Bureau Standards. He found at the time an agreement of about ±4 per ce between several American and German laboratories and the Reich anstalt. The only basis at present for agreement between the bure and the Reichsanstalt rests on a comparison recently made betwe the former and the Cleveland clinic which had been found to b within about 4 per cent of the Reichsanstalt.

Behnken's medium for transferring the unit was a carefully co structed ionometer with a magnesium thimble chamber and a uraniu oxide auxiliary radiation standard for controlling its sensitivity. A that time this was the best known means for effecting such a compar son, but later work—particularly that of Braun and Kustner [18, 19] an this laboratory [20, 21]—has proved it to be inadequate for the hig precision necessary. In a recent paper it was shown that while thimble chamber ionometer is sufficiently accurate for intensity mea urements in X-ray therapy it is liable to errors due to such factors

[7] A. Villard, Arch. d'Elec. Med., p. 692; 1908.
[8] Kroenig and Friedrich, Radiation Therapy; 1922.
[9] W. Duane and E. Lorenz, Am. J. Roent., **19,** p. 461; 1928.
[10] O. Glasser and V. V. Portmann, Am. J. Roent., **19,** p. 47; 1928.
[11] G. Failla, Am. J. Roent., **21,** p. 47; 1929.
[12] H. Kustner, Phys. Zeit., **28,** p. 797; 1927.
[13] H. Kustner, Strahlen., **27,** p. 331; 1928.
[14] L. S. Taylor, B. S. Jour. Research, **2,** p. 771; 1929.
[15] L. S. Taylor, B. S. Jour. Research, **3,** p. 807; 1929.
[16] L. S. Taylor, Radiology, **14,** p. 3; 1930.
[17] H. Behnken, Strahlen., **29,** p. 192; 1928.
[18] R. Braun and H. Kustner, Strahlen., **32,** p. 550; 1929.
[19] R. Braun and H. Kustner, Strahlen., **32,** p. 739; 1929.
[20] L. S. Taylor and G. Singer, B. S. Jour. Research, **4** (RP 169), p. 631; 1930.
[21] L. S. Taylor, Radiology, **15,** p. 227; 1930.

e "wall effect," [22] nonuniform distribution of ionization within the amber and the effective chamber length, all of which render such instrument incapable of the precision attainable with the standard. the various standards can not themselves be directly compared, the mparison instrument should have a precision at least as good as the ndards.

With this problem of agreement in mind, at the time the present imary standard was being developed, efforts were also directed ward the design of a readily portable secondary standard, the curacy of which would be equivalent to that of the primary.

II. CONSTRUCTION

In the design of a standard chamber, the fulfillment of certain ecessary requirements renders the instrument large and heavy. or example, the plate spacing must be sufficient so that a negligible umber of photo-electrons strike them, thus decreasing the amount measured ionization produced by a given beam. Duan,[23] Failla,[24] d Glasser[25] found for a parallell plate ionization chamber with the eam passing centrally between the plate that a spacing of 10 cm as sufficient. In order to permit the use of a wider beam of X rays, e standard chamber here used has a plate spacing of 12 cm.

The width of the guard plates must be about one and one-half to o times the plate spacing for this type of chamber[26, 27] in order at there be a perfectly parallel electric field across the whole width the collector electrode. Thus, for a plate spacing of 12 cm, the ards must be about 20 cm wide.

Also, if the plate system is to be inclosed in a grounded metal box r electrostatic and X-ray shielding, the spacing between the charged ate and box must be at least that of the interplate spacing.

On account of these considerations the present standard chamber necessarily very large and unwieldy. The cylindrical chamber sed by Behnken is a little less so, but not enough to permit transortation and field use.

It has not been found possible heretofore to decrease either the terelectrode spacing or the spacing between the electrodes and e grounded case. However, by means of a guard wire system, it as been found possible for a plate spacing of 12 cm to reduce the uard plate width from 18 to 5 cm and, likewise, the distance between igh potential electrode and grounded case from 12 to 3 cm.

This modified type of ionization chamber is shown diagramatically n Figure 1 from which it is seen that the guard plates are relatively arrow and the wall spacing small; whereas, ordinarily, such narrow uard plates would be entirely inadequate to insure a parallel field t the center of the chamber.

The field is rendered parallel by placing 10 small aluminum guard ires (a, b, c, – – –) across the ends of the chamber parallel to the lectrodes and about 1.1 cm apart, except for the center pair which re spaced about 1.6 cm apart. To each of these wires, beginning at

[22] L. S. Taylor and G. Singer, see footnote 20.
[23] W. Duane and E. Lorenz, Am. J. Roent., **19**, p. 461; 1928.
[24] G. Failla, Am. J. Roent., **21**, p. 47; 1929.
[25] O. Glasser and V. V. Portmann, Am. J. Roent., **21**, p. 47; 1929.
[26] G. Failla, Am. J. Roent., **21**, p. 47; 1929.
[27] L. S. Taylor, B. S. Jour. Research, **2**, p. 771; 1929.

the one nearest the guard, is applied a potential greater than that of the preceding wire by one-tenth the total voltage used to saturate the chamber. Thus, for 2,000 volts applied to the chamber, the wires (a, b, c, – – –) have potentials of 200, 400, 600, · · · volts. This is easily accomplished by a series of 11 one-half megohm resistors connected in series between ground and the high potential plate, the successive guard wires connecting successive resistors.[28] The electric field is thereby corrected as sketched in Figure 1.

Common grid-leak resistors may be used for the potential divider, provided they remain essentially constant with respect to each other. Wire-wound half-megohm resistors are more reliable but require more space. The potential of each wire was carefully checked with an electrostatic voltmeter and found to have the proper value.

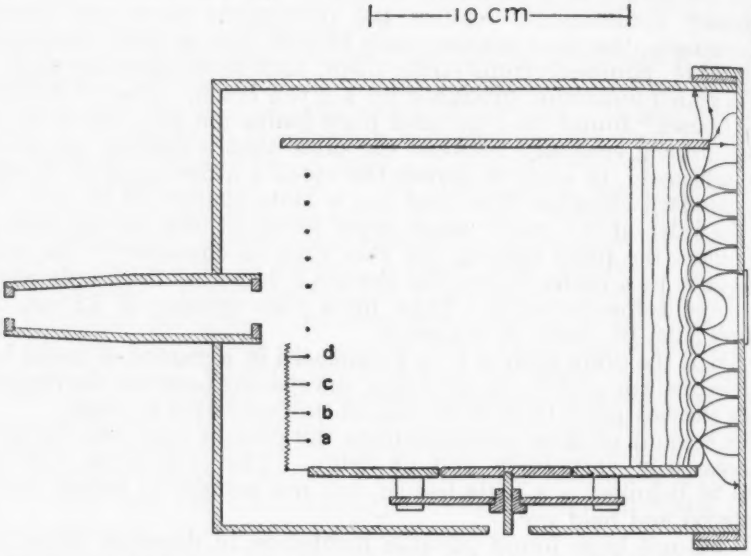

FIGURE 1.—*Diagrammatic cross section of ionization chamber showing some of the lines of force as affected by the guard wire system*

A photograph of the assembled electrode system is shown in Figure 2. In this the resistors are mounted on a hard-rubber sheet and the wires spaced on hard-rubber rods, the surface leakage of this material being negligible compared with that of the resistors. One of the four hard-rubber spacer rods may be replaced by a high resistance graphite rod and this used as the potential divider. Such a device, however, renders the chamber less rugged.

The electrode system is completely surrounded by a lead box braced with brass where necessary. Although this surrounding case is only 3 cm from the edges of the electrodes, this does not in any way affect the field within the chamber, since the potential wires provide sufficient field correction. Figure 3 shows this ionization chamber completely assembled with a flexile cable to connect to the electrostatic measuring system.

[28] This type of application of electrostatic shielding of the space between parallel plates at different potentials was first used by H. B. Brooks who developed the idea in 1916 and applied it to the design of an attracted disk electrometer. C. Snow, B. S. Jour. Research, 1 (RP17), p. 513; 1928.

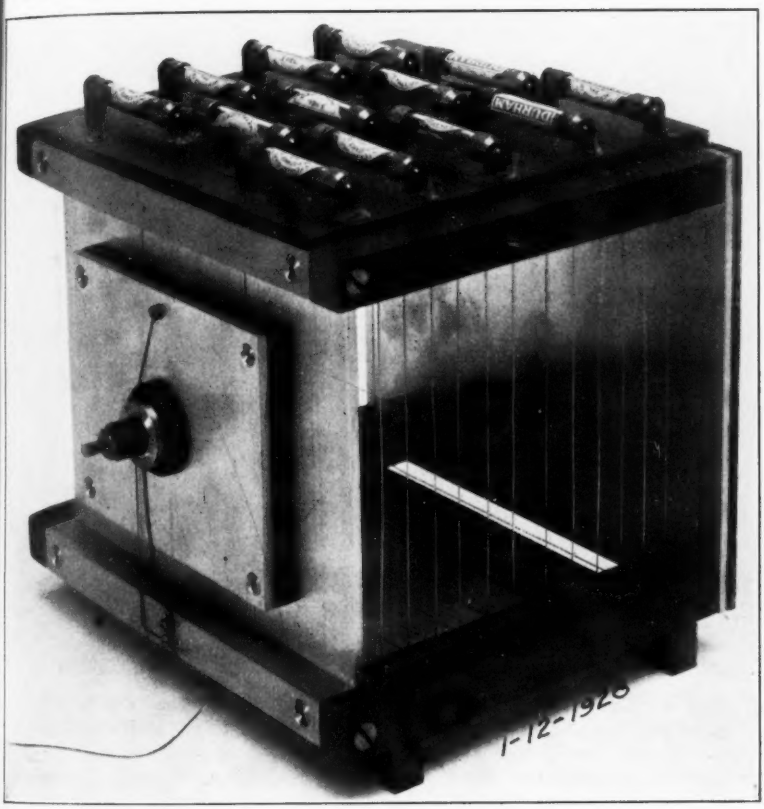

FIGURE 2.—*Assembled electrode system showing guard wires and potential divider*

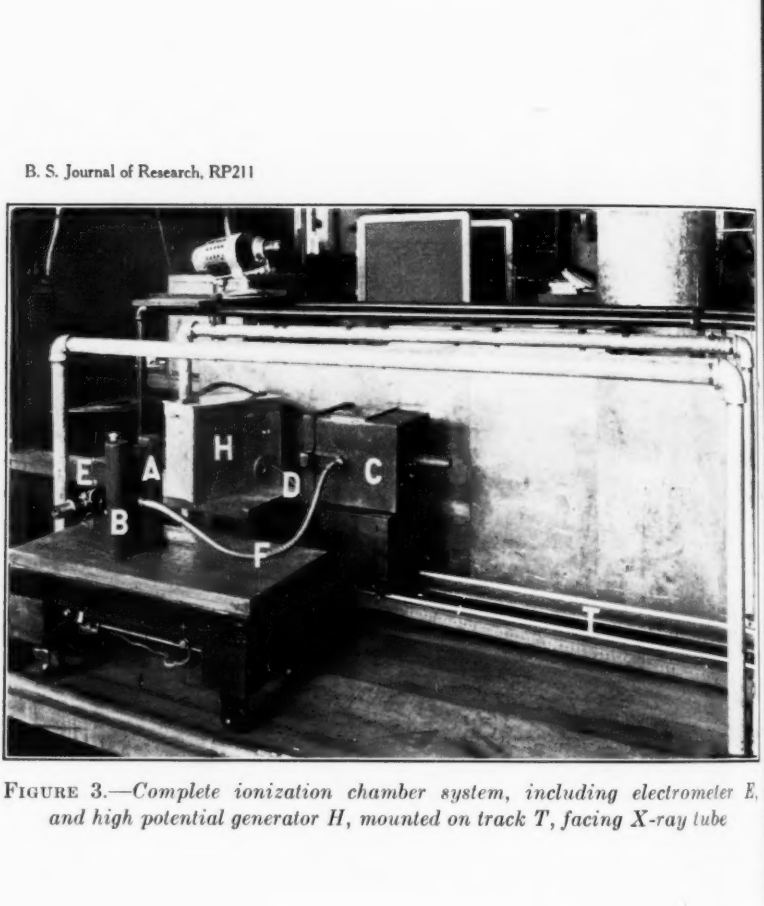

FIGURE 3.—*Complete ionization chamber system, including electrometer E, and high potential generator H, mounted on track T, facing X-ray tube*

The diaphragm system used with this is designed in accordance with that of the primary standard[30] and is held in place by a lead-lined brass tube which fastens to the front of the ionization chamber. The diameter of the limiting diaphragm is 0.8 cm so that the direct beam passing through the chamber does not strike any of the guard wires. At the inner end of the lead tube is a diaphragm 1.2 cm in diameter which minimizes the effect of any radiation scattered from the front diaphragm and the lead walls. At the back of the chamber the beam passes out through a 3-cm hole covered with a thin sheet of celluloid to eliminate air drafts.

The electrostatic measuring system is essentially the same as that used with the standard chamber and has been previously described in detail.[31] For field use, where the highest precision is not demanded, an idiostatic string electrometer system is used. The nature and magnitude of the error introduced through the use of this method has been previously investigated,[31] so that for the present needs the necessary correction can be made fairly closely. A portable idiostatic string electrometer, E (fig. 3) is connected directly to the

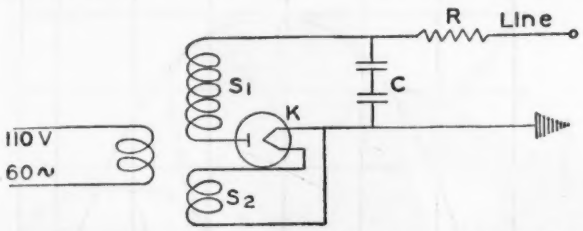

FIGURE 4.—*Diagram of portable kenotron rectified 2,200-volt generator*

ionization chamber, C, by means of a flexible cable, F. A and B are concentric cylinder condensers used for changing the sensitivity of the measuring systems.[32]

The potential used to saturate the chamber is supplied from a compact portable kenotron rectifier shown in figures 3 (H), 4, and 5. A low power 110-volt, 60-cycle transformer (R), specially built, is provided with two secondaries; S_2 to light the filament of a type H-1 kenotron K and S_2 to provide 1,550 volts rms which is rectified to give 2,200 volts d. c. In order to smooth out the rectified voltage, the capacitance, C, consisting of two 2 μf condensers in series, is inserted between ground and the high side. A protective resistance, R, of several megohms prevents an accidental dangerous flow of current. The voltage is led to the chamber by means of a rubber-covered cable, D (fig. 3), surrounded by a grounded copper "pigtail" sheath.

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[30] L. S. Taylor, B. S. Jour. Research, **3**, p. 807; 1929.
[31] L. S. Taylor. See footnote 27, p. 507.
[32] A current-balancing null system was first employed, using for this purpose a uranium oxide ionization chamber in which the ionization current was adjusted by a large iris diaphragm placed about 1 mm from the uranium oxide covered plate. Since then Failla [33] and Jaeger [34] have devised better forms of ionization compensators; hence, it is planned in the future to use a radium-compensating chamber devised and very kindly furnished us by Dr. Failla. This system provides a wide range of currents and lends itself well to transportation with unaltered calibration.
[33] G. Failla (seen in MS. form. Read at Toronto, Dec. 3, 1929).
[34] R. Jaeger, Strahlen., **33**, p. 542; 1929.

III. ADJUSTMENT AND ALIGNMENT

From the foregoing it is evident that the chamber closely resembles the standard chamber already described.[35] This is highly desirable since it makes the conditions of alignment and diaphragming identical for the two and consequently minimizes uncertainty due to corrections which must otherwise be made.

As with the primary standard, the alignment with respect to the X-ray tube is fairly critical. For experimental test the chamber was mounted on a 2 m track, T (fig. 3), placed parallel to the X-ray beam and pivoted so as to rotate horizontally about its center. Lateral adjustment in the X-ray beam is effected by moving the X-ray tube. (For field use the chamber is mounted on a short track providing the lateral motion.)

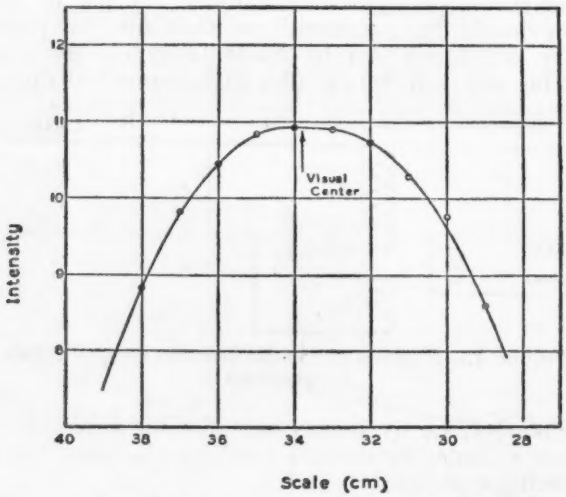

FIGURE 6.—*Cross section of beam to obtain lateral alignment of ionization chamber*

Preliminary visual alignment of the ionization chamber is made by sighting through the diaphragm system at the focal spot. This is facilitated by a cross line marked on the celluloid window at the back of the chamber. With the small focus X-ray tube, such adjustment is fairly accurate as shown in Figure 6, but it has been found unsafe to rely upon this method alone, particularly when used with a broad-focus tube. In all cases ionization readings are made successively as the X-ray tube is shifted laterally in a direction at right angles to the beam, and thus a measure of the intensity distribution across the beam is obtained. The final position of the chamber is that corresponding to the center of the intensity distribution peak. Likewise the chamber is tested for its angular alignment by measuring the ionization as it is rotated through a small angle about its center. Visual centering is more reliable in this case. Figure 7, showing the ionization intensity as the chamber is rotated, indicates the small range of adjustment possible; even

[35] L. S. Taylor. See footnotes 14 and 15, p. 508.

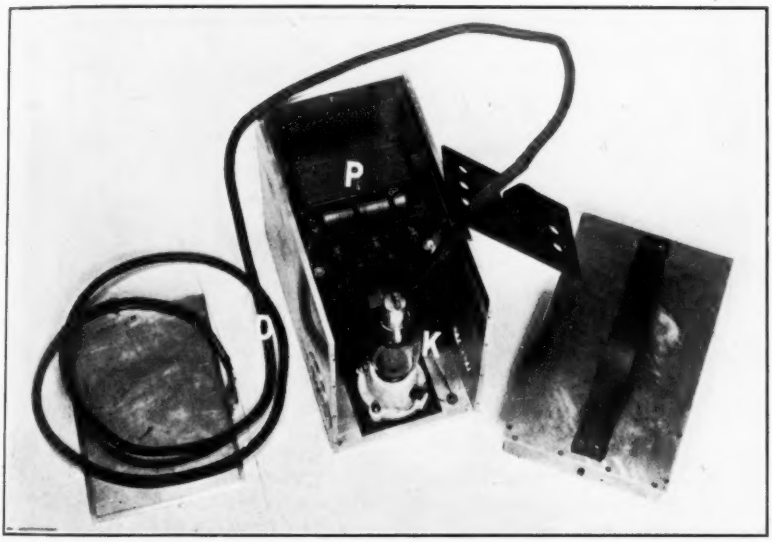

FIGURE 5.—*2,200-volt D. C. kenotron rectifier unit (cut away to show construction)*

ith a fairly broad beam a rotation of over 1° in either direction will use an error in the measurements.

For studying the behavior of this chamber, two X-ray tubes of e 200 kv Coolidge deep therapy type were employed. The first d a fine, very closely defined focal spot, while the second had a oad, poorly defined focal spot with a "black center," these selecons representing the two extremes ordinarily encountered in practice. easurements with the standard chamber revealed a strict adherence the inverse square law of intensity for the first tube and to the verse 2.1 power for the second.

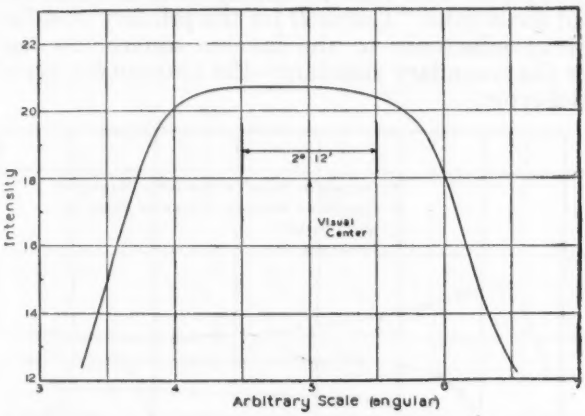

FIGURE 7.—*Cross section of beam to obtain angular alignment of ionization chamber*

IV. PERFORMANCE

To be certain that the potential wires provided proper field correcon, saturation conditions were studied as for the primary standard amber; four different measuring methods were used for which the turation curves are shown in Figure 8. Curve *A* is for a system in hich the collector plate is allowed to discharge to a potential below at of the guard electrodes; Curve *B* for a collector charging above e guard potential; Curve *D* for an idiostatic measurement, and for a null compensation measurement. It is seen from these rves that the behavior is almost identical with that of the primary andard chamber using wide guard electrodes. [36]

The extent to which radiation was scattered from the diaphragms d potential wires was next investigated. A photographic film aced against the wires at the back of the chamber showed no adow whatever of the wires after a long exposure with the aligned eam passing through the chamber. This indicates that scattering om the wires is negligible.

The second diaphragm used to reduce the effect of scattering from e limiting diaphragm is necessary as shown by the inverse square w curves. (Fig. 9.) Curve *A* shows for the standard chamber, e logarithm of the intensity as a function of the logarithm of the stance measured between the focal spot of the broad focus tube

[36] L. S. Taylor, see footnote 14, p. 508.

and the front of the chamber diaphragm, which was set at the sa diameter (0.8 cm) as that of the secondary chamber under investig tion. From the slope of this plot it is found that the intensity obe the inverse 2.1 law. Repeating the same observations with t secondary standard, curve *B* was obtained, showing a close paral to the standard chamber within the experimental error. The sc tering diaphragm, *S* (fig. 1), was then removed from the back of t lead tube and, again repeating the run, curve *C* was obtained, sho ing a marked divergence from the results obtained with the standa chamber. The need of the back diaphragm, *S*, is thus clearly evide

The observations were next repeated, using the fine focus inste of the broad focus tube. Curve *D* for the primary standard chamb shows a strict adherence to the inverse square law, and likew curve *E* for the secondary standard—the two curves agreeing wit experimental error.

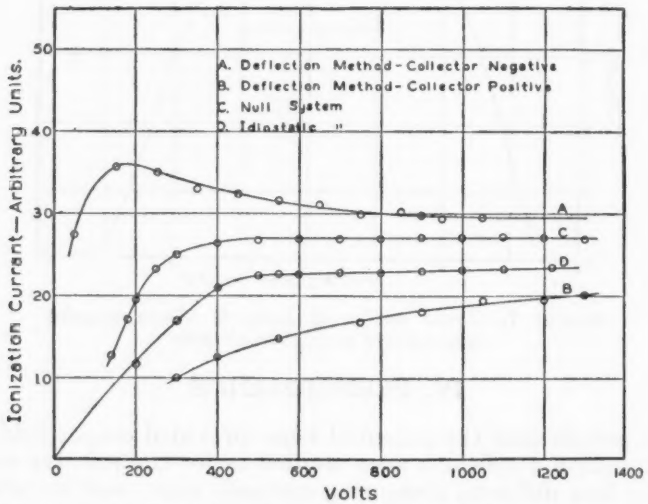

FIGURE 8.—*Saturation curves for new ionization chamber as obtained by four methods*

These are almost identical with saturation curves for the large standard chamber.

The final measure of accuracy obtainable with the chamber is a direct comparison with the primary standard chamber. To ru out any differences in the two electrometer systems for preliminar measurements, the same electrometer and compensating system w used for both chambers without necessitating any changes whatev in either the system or its connections. Both chambers were charg by the same source of high potential; in making observations, it w only necessary to shift the tube from one chamber to the other a matter of about half a minute.

The effect of altering the size of the limiting diaphragm next the X-ray tube was investigated, maintaining both chambers at t fixed distance of 75 cm from the target. These data show that t two chambers fluctuate in the same manner, due to the unev distribution of energy over the focal spot and off-focus radiation.[37]

[37] L. S. Taylor, B. S. Jour. Research, 3, p. 807; 1929.

Table 1 summarizes the data obtained. Column 2 gives the r/min. measured with the primary standard chamber and column 3 the percentage mean deviation of the observations made for each point. Likewise columns 4 and 5 give, respectively, the r/min. and the mean deviation of observations made with the secondary chamber. Column 6 shows the percentage agreement in the r/min. as measured with the two chambers, indicating that, in general, the agreement is within the observational error. All of the measurements thus far have been made with the same null electrostatic measuring system.

The final check was made using two entirely separate electrostatic current measuring systems. A few of the measurements taken under random conditions are shown in Table 2, which needs no explanation.

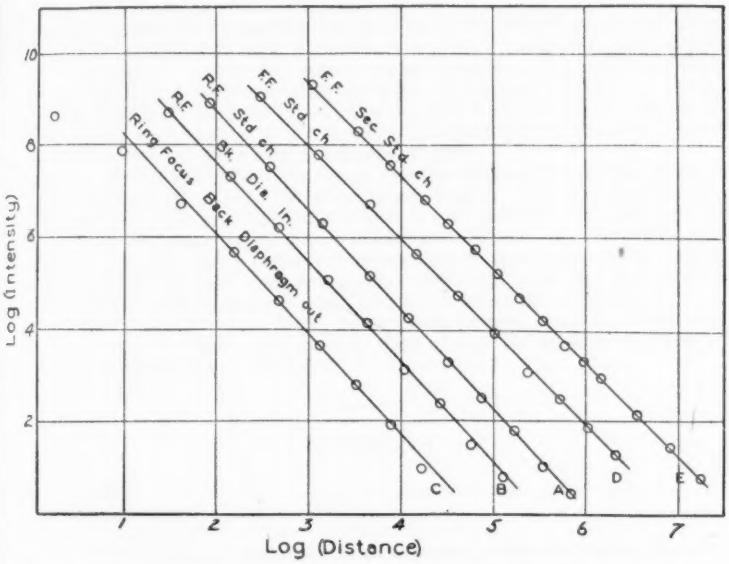

FIGURE 9.—*Inverse square law curves for primary and secondary standard chambers*

Logarithms shown are only to give slope and do not apply directly to the experimental points shown.

TABLE 1

Diameter of tube diaphragm	r/min. primary standard	Deviation	r/min. small standard	Deviation	Difference
1	2	3	4	5	6
		Per cent		*Per cent*	*Per cent*
20	33.1	±0.2	32.6	±0.4	−0.7
18	32.8	.2	32.8	.1	.0
16	32.8	.3	33.0	.1	+.3
14	32.6	.2	32.6	.5	.0
12	31.6	.2	31.6	.3	.0
10	30.0	.2	30.4	.3	+.6
8	24.2	.2	24.3	.2	+.2
6	18.8	.2	18.6	.0	−.5
4	9.9	.2	9.9	.1	.0
Average difference					±.26

TABLE 2

Primary standard			Secondary standard			
Tube distance	Chamber diaphragm	r/min.	Tube distance	Chamber diaphragm	r/min.	Agreement
cm	*cm*		*cm*	*cm*		*Per cent*
94.5	0.8	14.00	94.5	0.8	14.25	±0.8
94.5	.8	5.24	94.5	.8	5.26	±.2
87.2	.8	6.23	87.2	.8	6.18	±.4

WASHINGTON, March 1, 1930.

ABSORPTION MEASUREMENTS OF THE X RAY GENERAL RADIATION

By Lauriston S. Taylor

ABSTRACT

Studied as a means for indicating the quality of the radiation, copper absorption curves for heterogeneous X rays were obtained, using a standard and two thimble ionization chambers. With the standard air chamber, logarithmic absorption curves were not found to become straight for filters up to 3 mm in thickness—indicating a gradual elimination of the longer wave lengths. With thimble chambers, owing presumably to errors from the chamber "wall effect," the curves were nonlinear only up to 1 mm thickness of filter.

Half-value layers and effective wave lengths derived from the three sets of results were compared. The "effective wave length" as derived from the slope of the absorption curve and the "half-value layer" are about equally sensitive to changes in quality at least up to 3 mm thickness of filter. As should be expected, effective wave lengths thus obtained are always longer than those obtained by Duane's finite filter method and, being less dependent upon the particular instrument used in the measurements, are, therefore, more consistent.

On the basis of the effective wave-length determinations it is found that, contrary to the accepted views, the greater part of the highly filtered energy is not concentrated in the tungsten K lines.

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I. INTRODUCTION

In connection with the proper control of X radiation in its various applications, reliable and relatively convenient means of measuring the radiant energy is the first necessity. This part of the problem seems to be satisfactorily solved by observing proper care in the design and use of the ionization chamber. The bureau has, therefore, announced its completion of a standard ionization chamber.[1] The next

[1] To be published in April issue of Radiology and March issue of American Journal of Roentgenology.

project on this program is the study of possible methods of determining "quality" of radiation. The accuracy with which it is necessary to describe the quality depends, of course, upon the particular use to which the radiation is put. In radiological practice an accuracy of 3 to 4 per cent may be sufficient, whereas in precise physical experiments the accuracy should be better as indicated, for example, in the recent papers by Compton,[2] and Crowther and Bond.[3]

In the radiological field recent work by Pohle and Barnes,[4] Quimby and Burby and Barry [6] has shown large discrepancies in the quality of the different X-ray beams as measured by different methods. Moreover, Quimby showed that three beams having the same "quality" according to some method A, had radically different "qualities" according to another method B. It thus appeared desirable to make a fairly comprehensive study of available methods and the devices used in applying them.

Inasmuch as a beam of X rays may cover a range of wave lengths which are unequally effective in producing the results sought, next in importance to measuring the total energy is that of determining the distribution of the energy among the wave lengths present. The direct measurement of spectral energy distribution is the most reliable and satisfactory way of describing the quality of the radiation, but this is so difficult and cumbersome that the method eliminates itself from the field of practical applications. Fairly sound substitute methods of greater utility have been based on the degree of absorption of the total energy by filters of standard materials (copper, silver, aluminum, etc.), knowledge of the incident radiation being inferred from the absorption measurements of various filter thicknesses.

Even if the ionization spectrometer method of mapping the spectral radiation were not so difficult and cumbersome under present conditions, it would still be far from an ideal method owing to the many conditions involved, some of which are not well understood. The more common forms of the X-ray spectrograph as substitute for the ionization spectrometer are inadequate, for, due to such factors as X-ray scattering, photographic halation and spectral sensitivity of the emulsion, a simple density curve of the photographic plate may be very misleading. In using such data to determine minimum wave length,[7] it is necessary to extrapolate the curves to zero energy by starting at some point well up on the established curve, which, of course, makes for very uncertain conclusions.

With these facts in mind the best method, for practical purposes, for arriving at the quality of any given X-ray beam seems to be that involving direct absorption measurements.

In deep therapy wave-length ranges, Duane has shown that absorption measurements in copper are well suited for describing the quality.[8] In the superficial therapy range, either copper or aluminum absorption measurements [9] may be used; and, in the "Gren

[2] A. H. Compton, Phil. Mag., **8**, p. 961; 1929.
[3] J. C. Crowther and W. N. Bond, Phil. Mag., **6**, p. 401; 1928.
[4] E. A. Pohle and J. M. Barnes, Radiology, **10**, p. 300; 1928.
[5] E. H. Quimby, Am. J. Roent., **21**, p. 275; 1929.
[6] J. J. Burby and M. W. Barry, Radiology, **12**, p. 275; 1929.
[7] A. Mutscheller, Radiology, **12**, p. 283; 1929.
[8] Wm. Duane, Am. J. Roent., **9**, p. 167; 1922.
[9] Wm. Duane, Am. J. Roent., **20**, p. 241; 1928.

rapie" range, most observers have used very thin aluminum orbers.[10, 11, 12]

In their technical production, various types of high voltage gen- tors are used, many having a characteristic wave form and, hence, mishing X rays of periodically varying quality. If the peak volt- of such a generator remains constant, however, the radiant ergy at all wave lengths integrated over any practical interval of ne, will be proportional to that interval; and the resulting spectral ergy distribution may be treated as constant. This is not merely obvious assumption, but is supported by experience in that it s been found that essentially the same quality of radiation may be tained from mechanical rectifiers as from constant potential sources the rectifier be operated at a slightly higher peak voltage than the nstant voltage source.

The present study has been confined throughout to a practically nstant potential source,[13] inasmuch as this makes for more ready finition of the spectral energy distribution.

II. THEORY OF ABSORPTION MEASUREMENTS

1. ABSORPTION OF HETEROGENEOUS RADIATION

Representing by E_λ the energy between the wave lengths λ and $+d\lambda$ of the beam, the total energy (E) of a continuous X-ray ectrum, void of characteristic lines, may be expressed as an inte- al between the short wave length limit $\lambda=\lambda_o$, and $\lambda=\infty$; that is,

$$(E)=\int_{\lambda_0}^{\infty} E_\lambda \, d\lambda \tag{1}$$

the form of E_λ is known the total energy (E) may be calculated. he magnitude of E_λ as it varies with λ has been derived theoretically Behnken [14] who found fair agreement between his theoretical and lrey's [15] experimental curves for constant potential X rays. A ore recent combined experimental and theoretical study by Kulen- ampff [16] has revealed even better agreement between theory and periment. In the present work we are concerned, however, with e problem of deducing some knowledge of the spectral distribution , from measurements of the total energy (E) after passage through roperly chosen filters.

If a filter of thickness x intercept a beam of radiation, the incident nergy E_λ comprised between the wave lengths λ and $\lambda+d\lambda$ will be educed by the filter to a quantity of energy E'_λ, emerging from the lter, of a magnitude given by the well-known equation

$$E'_\lambda = E_\lambda \, e^{-\mu_\lambda x} \tag{2}$$

here μ_λ is the "absorption coefficient" of the material of the filter r the radiation of wave length λ. Here, of course, scattering is eglected.

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[10] O. Glasser and U. V. Portmann, Am. J. Roent., **10**, p. 442; 1928.
[11] H. Kustner, Strahlen., **27**, p. 124; 1927.
[12] L. E. Jacobson, Am. J. Roent., **22**, p. 544; 1929.
[13] L. S. Taylor, B. S. Jour. Research, **2** (RP56), p. 771; 1929.
[14] H. Behnken, Zeit. f. Phys., **4**, p. 241; 1921.
[15] C. T. Ulrey, Phys. Rev., **9**, p. 548; 1917.
[16] H. Kulenkampff, Ann. der Phys., **69**, 548; 1922.

The value of μ_λ for copper or other material may be obtained fro tables or computed from Richtmyer's [17] formula for the "mass a sorption coefficient" $\frac{\mu_\lambda}{\rho}$, in which

$$\mu_\lambda/\rho = A\lambda^3 + K \tag{3}$$

A and K being constants for the given material and ρ the density the material.

For copper between $\lambda = 0.12$ and 0.30 angstroms, Richtmyer found

$$\mu_\lambda/\rho = 153\lambda^3 + 0.2 \tag{3a}$$

λ being expressed in angstroms and μ in cm $^{-1}$.

From an inspection of equation (3) it is obvious that any filter i serted in a heterogeneous beam will absorb the longer wave length more than the shorter and, hence, "harden" the radiation. Th means is used in practice. Furthermore the degree of hardness the radiation transmitted by any given filter may be indicated b the extent to which a second additional filter inserted in the bea absorbs the radiation transmitted by the first. It is this applicatio with which we are here concerned.

2. APPLICATION OF ABSORPTION MEASUREMENTS IN DESCRIBIN X-RAY QUALITY

(a) EFFECTIVE WAVE LENGTH

One method, which makes use of absorption measurements f obtaining an indication of the quality of an unknown heterogeneou radiation of energy (E), is that which determines the wave leng of the homogeneous radiation which would be reduced in intensit by a given filter in the same degree as the heterogeneous radiati is reduced by it. The heterogeneous radiation is then designated having an *effective wave length* equal to that of its correspondi homogeneous radiation.

For example, relation (2) relates the transmitted to the incide radiation of wave length λ through the thickness of the filter x a the absorption coefficient μ_λ.[19] Taking now the incident and tran mitted heterogeneous energies (E) and (E') we may use a *compos absorption coefficient* [20] μ, such that

$$(E') = (E)e^{-\mu x} \tag{4}$$

Having the values of μ_λ, either from tables or equation (3a), eith (E) or (E') may be said to have that effective wave length λ_e f which

$$\mu = \mu_\lambda \tag{4a}$$

or, if x be taken sufficiently small, both may be assigned the eff tive wave length in question.

Duane uses a filter of given material and of finite thickness x f obtaining the effective wave length of the radiation incident thereon.

[17] F. K. Richtmyer, Phys. Rev., **18**, p. 13; 1921.
[18] F. K. Richtmyer and F. W. Warburton, Phys. Rev., **6**, p. 539; 1923.
[19] L. S. Taylor, Radiology, **12**, p. 289; 1929.
[20] A. H. Compton, X Rays and Electrons.
[21] W. M. Duane, Proc. Nat. Acad., **13**, p. 668; 1927.

The results of a comparative experimental study of this, and that of an infinitesimal thickness of filter with different available devices for measuring the energy of the beam, was the partial object of the present investigation.

Illustrations of the two methods of determining effective wave lengths are to be found in Figures 1 and 4 where, with increasing thickness of filter, the logarithm of the transmitted energy is plotted against thickness of a given filter material. Let in equation (4),

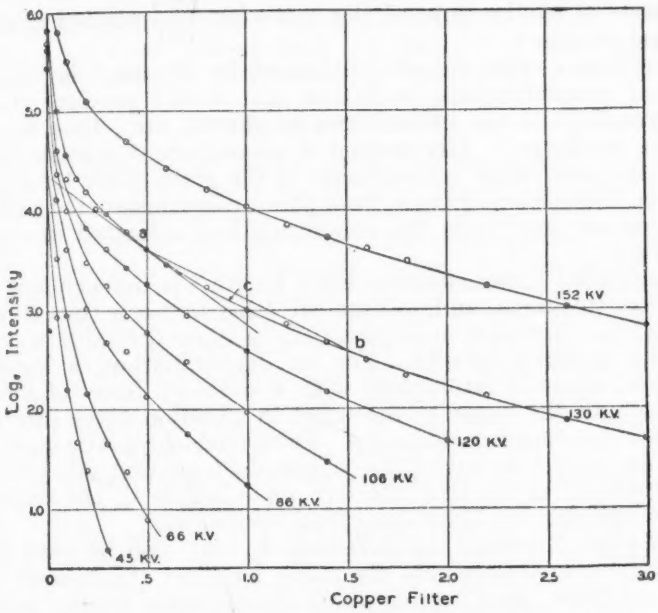

FIGURE 1.—*Copper absorption curves made with standard air ionization chamber for practically constant voltage X rays*

(E') be the energy at any thickness x', and (E'') that at a thickness $x''=x'+x$; then Duane's method applied gives

$$(E')=(E)e^{-\mu' x'} \tag{5}$$

$$(E'')=(E)e^{-\mu'' x''} \tag{6}$$

From this

$$\log\frac{(E')}{(E)}-\log\frac{(E'')}{(E)}=\mu''\,x''-\mu'\,x' \tag{7}$$

Noting that μ' in equation (5) depends on the entire thickness x', and μ'' in equation (6) depends on the same thickness of filter plus the increase $x=x''-x'$, it appears at least approximately correct within limited ranges to use an intermediate value of μ such that

$$\mu=\frac{\log\frac{(E')}{(E)}-\log\frac{(E'')}{(E)}}{x} \tag{8}$$

Here μ is dependent upon x as well as upon (E') and (E''). If however, x be taken small enough, equal to Δx, so that the filter does not appreciably change the quality of the radiation passing through it, and yet produces a measurable change in the energy of the beam then

$$\mu = \frac{\Delta \log \frac{(E')}{(E)}}{\Delta x} \qquad (9)$$

is represented by the slope of the curve $\log \frac{(E')}{(E)}$ plotted against the thickness of filter x.

The effective wave length as defined by Duane [22] is "the wave length of monochromatic radiation that would produce the same effect (readings of the instruments employed, etc.) that the actual radiation produces." His method of measurement consists in determining the percentage transmission of the given filter for the given radiation, then determining λ_e from previously constructed calibration curves, as obtained from the absorption law indicated in equations (2) and (3).

The so-called "true effective wave length" is independent of any given filter thickness; and, in that one other factor is thus eliminated from its determination, it is physically a more desirable way to express the quantity sought. For its determination, a logarithmic absorption curve is established with a series of filters of increasing thickness and the slope at the point in question gives directly the composite absorption coefficient μ. From monochromatic wave-length absorption curves or Richtmyer's formula (equation (3a)) may thus be determined, as the true effective wave length λ_e, the single wave length which has the same absorption coefficient.

A "bracket" method for obtaining λ_e may also be used wherein two intensity measurements are made for filter thicknesses equally above and below the filter for which the radiation quality is desired. The absorption coefficient and corresponding λ_e is then obtained from the difference of the logarithms of these two intensity measurements, it being assumed that this absorption coefficient is the same as that corresponding to the intermediate filter. Such a method, while nearer the tangent method (true λ_e) than Duane's, does not make full allowance for the curvature of the logarithmic absorption curve between the points taken.

The bracket method is exactly the same as Duane's method as far as the operational procedure is concerned, except that the radiation for which λ_e is determined corresponds more nearly to that of the intermediate filtration instead of the smaller filtration. By Duane's method the ratio of the two intensities $(E')/(E'')$ for filtrations x' and x'' is said to give λ_e for the filtration x' whereas the bracket method gives λ_e for a filtration close to $(X' + X'')/2$. As shown later, the difference between the two varies according to the range in which the measurements are applied, and may be neglected for many practical purposes.

In Duane's earlier work he specified the use of 1 mm of copper for obtaining the effective wave length. The use of such a large filter-difference will give reasonably consistent agreement with the true λ_e

[22] Wm. Duane, Am. J. Roent., 20, p. 241; 1928.

only for very high filtrations as shown in Table 2 and when used according to the bracket method (equation (8)). For lower filtrations the differences between the two methods increases. In later work he specified the use of 0.25 mm filter separation, thus increasing considerably the range over which λ_e might be determined with fair agreement with the other method (true λ_e).

Duane also indicated at the time that small errors in the measurement of filter thickness may cause an appreciable error in the determination of λ_e by his method. The effect on λ_e of errors in thickness will, of course, be greater for the method using 0.25 mm filter separation than for the 1 mm method. In the case of obtaining λ_e from a complete absorption curve such errors are averaged out.

(b) HALF-VALUE LAYER

One of the earliest methods of describing the quality of a heterogeneous X-ray beam was to measure the absorption by a series of filters of some material and then determine from the absorption curve the thickness of that material which would reduce the intensity of the given beam to one-half its initial value. If, for example, a beam has an intensity of E_{F_1} after passing through a filter of thickness x_1, and E_F, is the half-intensity ($E_{F_1}/2$) after passing through a filter x_1+x_2, then x_2 is the half-value layer of the particular material for that radiation which has passed through x_1. While then the quality is expressed by the effective wave length as determined by a given thickness of filter of given material, the half-value method expresses the quality in terms of the thickness of filter (of given material) required to reduce the intensity by a given amount (one-half).

Obviously, the shorter the effective wave length of the given radiation, the thicker this half-value layer of filtering material must be. Inasmuch, therefore, as the composite absorption coefficient μ of equation (4) varies with the thickness x of the added filter, there is no simple direct quantitative relation connecting effective wave length with half-value layer.

Comparing the half-value layer and effective wave-length method, the latter has the advantage in that it presents a clearer physical picture of the radiation quality.

In Roentgenological practice, the voltage wave forms are usually of two general types, being either approximately constant or approximating a sine wave; and the target material is always tungsten. Here the "half-value" method has served as a useful approximation for expressing the radiation quality. However, as a particular example, it is unsafe to rely on this method for comparing qualities of two radiations, one excited by constant and the other by a fluctuating voltage. Quimby [23] made a detailed study of the qualities of various radiations, all having the same half-value layer of copper, and found large differences between them.

The inset (A) in Figure 5 shows a plot of the half-value layer taken from the absorption curve in Figure 5, for filtrations as high as 1.6 mm of copper. Investigations cited [24] have indicated that such a curve would be different for each voltage wave form applied to the tube.

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[23] E. Quimby, Am. J. Roent., **21**, p. 64; 1929.
[24] See footnotes 4, 5, 6, and 29.

(c) AVERAGE WAVE LENGTH

This method was proposed by Mutscheller [25] several years ago. It follows the true effective wave-length method in that from the tangent to a heterogeneous radiation absorption curve a coefficient of absorption is determined from Richtmyer's tables with which the corresponding monochromatic wave length is identified. He definitely divides his measurements into two classes, those for the portion of the absorption curve from zero to the "homogeneity filter" [26] and those beyond this point.

According to the results presented in this paper there can be no "homogeneity filter," strictly speaking. Practically a filtration may be reached beyond which the radiation quality changes comparatively little—the absorption curve approaching linearity.

In most of his published absorption curves he shows such linearity above about 0.5 mm copper filtration, indicating the attainment of effectively homogeneous radiation. There is no evidence that such a condition should be rigidly true and it is not reached within the range of filtration (0 to 3 mm Cu) used in this paper. It appears, therefore, that the average wave lengths so obtained in the region beyond the "homogeneity filter" are subject to errors larger than herein contained; that is, Mutscheller's method is that of the true effective wave length above but applied in the range where the errors are such as to render the results questionable. Applied in the region below the "homogeneity filter"—that is, for small filtrations—his method is identical with the so-called true effective wave-length method.

III. EXPERIMENTAL RESULTS

1. COMPARISON OF DIFFERENT IONIZATION CHAMBERS

In the development thus far we have dealt with ideal conditions wherein it has been considered possible to make direct energy measurements. However in applying absorption measurements as an indication of the quality of a given X-ray beam, the ionization current produced by the beam is the quantity measured. The current per unit energy does not change rapidly with wave length, and for simplicity we will speak of this as energy, understanding, of course, that the measured ionization is proportional to the energy absorbed from the beam by the air in the ionization chamber.

The results of absorption measurements made by a number of observers are not in close agreement; consequently the technique of making such measurements has been studied in the greater detail given here.

In some recent work at this laboratory a study was made of the calibration of the thimble ionization chambers against a standard air ionization chamber [27] in which it was brought out that there was a marked difference in the copper absorption curves for the same radiation when measured with several different thimble ionization chambers and the standard chamber.

In Figure 1 is shown a series of semilogarithmic copper absorption curves obtained by measuring the incident and transmitted intensities

[25] A. Mutscheller, Radiology, May, 1924; October, 1924; April, 1929.
[26] E. A. Pohle, Radiology, **10**, p. 300; 1928.
[27] L. S. Taylor and G. Singer, B. S. Jour. Research, **4**, (RP169) p. 631, May; 1930.

with the standard air ionization chamber. The tungsten X-ray tube was operated at practically constant potential as recently described. The diaphragming system [28] to limit the beam was in accordance with the necessary conditions to make an accurate determination of the effective intensity of the beam in Roentgens.[29] When a thimble ionization chamber was used, it also was in accordance with previously described technique.[30, 31] The configuration of the system in Figure 2 shows the arrangement diagrammatically, and is self-explanatory.

For the curves shown in Figure 1 the diaphragms M and N each had a radius of 12 mm and the interdiaphragm distance B was 65 cm. The filters were 15 cm from M, thus making the distance C between filter and chamber diaphragm 50 cm. In taking this data the precision of observation for a single filter was about ± 0.2 per cent. The copper filters had a tested purity of 0.99998 and their thicknesses were uniform to within ± 0.002 mm. It is clearly evident that for the curves shown there is no straight portion up to a copper filtration of 3 mm, although it is apparent that they are asymptotically

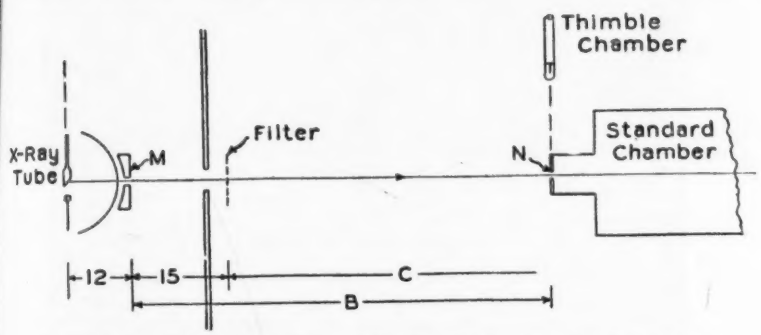

FIGURE 2.—*Diagram of X-ray tube-filter-ionization chamber system*

approaching a straight line. A large number of other such curves were obtained under varying conditions of the distance B and the diaphragms M and N, and all were exactly similar to those shown.

In order to be certain that no peculiarity of this system could be responsible for the form of these curves, I have obtained through the courtesy of Dr. Failla and of Dr. Quimby, of Memorial Hospital, New York, N. Y., the set of absorption curves for tube potentials up to 200 kv, shown in Figure 3. These were made some months previously with a thimble air wall ionization chamber differing slightly in construction from that used at the bureau. Here also it is clearly evident that the absorption curves do not become straight.

Attention may also be called to a paper by Rump,[32] in which is given a similar series of absorption curves for potentials up to 150 kv (fig. 5 in his article). Again, it is found that the curves are non-rectilinear. In view of the excellent agreement of these different workers there seems no question of the validity of the results.

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[28] L. S. Taylor, B. S. Jour. Research (RP56), **2**, p. 771; 1929.
[29] L. S. Taylor, B. S. Jour. Research (RP119), p. 807; 1929.
[30] See footnote 28, p. 524.
[31] L. S. Taylor, Radiology, **15**, 227.
[32] W. Rump, Zeit. f. Phys., **43**, p. 254; 1927; **44**, p. 396; 1927.

The same type of copper-absorption measurement was next mad with several thimble ionization chambers placed at various distance from the filter, but all for the same beam of radiation. It must b pointed out that the precision of observation with such chambers i not as great as with a standard air chamber, and consequently we ca not place the same reliance on the measurements made with them.

In order to be certain that the position of the ionization chambe with respect to the filter did not influence the measurements, a serie of intensity readings were made keeping the chamber fixed and chang ing the filter position. For the standard ionization chamber n measurable effect was produced by moving the filter from 0.5 to 3 cm from the entrant diaphragm. However, shifting the filter ove the same range for a thimble chamber, the measured intensity fell o

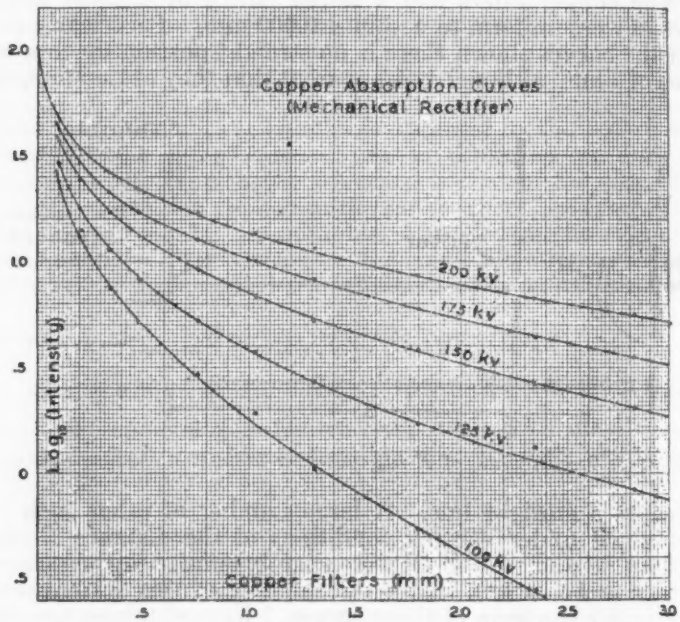

FIGURE 3.—*Copper absorption curves made for mechanically rectified voltage*

steadily up to a distance of about 10 cm where it reached a steady value. Consequently, all measurements with a thimble chamber were made at least 15 cm from the filter.

In Figure 4 are shown three semilogarithmic absorption curves: *S*, obtained with a standard; *G*, with a Glasser thimble chamber, and *F* with a Friedrich thimble chamber. The X-ray tube was operated at 133 kv, d. c., for all. The standard chamber was set 45 cm from the filter and the Glasser chamber and Friedrich chamber at about 15 cm.

The original data for these curves are given in Table 1. The intensities I_F and I_G, as measured with the Friedrich and Glasser chambers, respectively, have each been corrected for a very small natural leakage. There was no measurable leakage in the standard chamber system. Half-value layers obtained from this data were in

ood agreement with Holthusen's curves for the voltage used,[33] both easurements being made with a standard chamber.

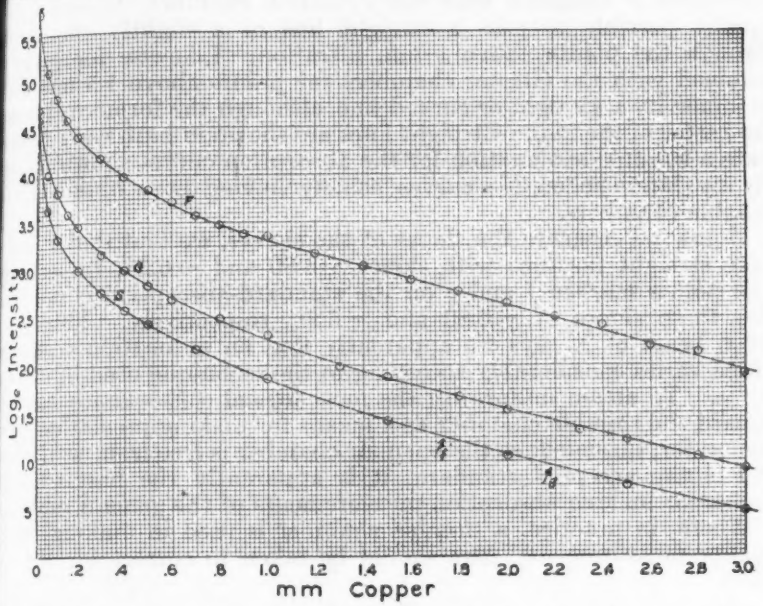

FIGURE 4.—*Copper absorption curves made for 133 kv radiation, using three different chambers*

TABLE 1.

Filter	Standard		Friedrich		Glasser	
	I_S	$\log_e I_S$	I_F	$\log_e I_F$	I_G	$\log_e I_G$
1	2	3	4	5	6	7
0	100.0	4.60	312.0	5.74	111.0	4.71
.05	38.4	3.65	164.0	5.10	55.7	4.01
.1	28.6	3.355	123.0	4.81	45.4	3.82
.15			99.0	4.58	35.7	3.58
.2	20.0	3.00	81.6	4.40	30.4	3.46
.25	(17.8)		72.6	4.285	(26.8)	
.3	16.1	2.78	66.3	4.194	23.8	3.16
.4	13.0	2.565	53.6	3.98	20.0	3.00
.5	11.5	2.44	48.1	3.87	17.2	2.84
.6			41.2	3.72	14.8	2.69
.7	8.70	2.16	35.6	3.57	(13.4)	
.8			32.5	3.48	12.1	2.495
.9			29.8	3.39		
1.0	6.49	1.87	28.8	3.36	10.2	2.315
1.2	(5.4)		23.6	3.16	(8.4)	
1.3					7.35	1.99
1.4			20.8	3.035		
1.5	4.11	1.43	(19.4)		6.62	1.89
1.6			18.0	2.89		
1.8			15.8	2.76	5.26	1.66
2.0	2.86	1.05	14.2	2.65	4.58	1.52
2.2			12.2	2.50		
2.3					3.72	1.31
2.4			11.2	2.42		
2.5	2.08	.733			3.36	1.21
2.6			9.0	2.20		
2.8			8.5	2.14	2.84	1.04
3.0	1.60	.469	6.7	1.90	2.56	.714

[33] H. Holthusen, Radiology, **10**, p. 292; 1928.

It is seen that the curve obtained with the standard chamber do not become straight for filtration up to at least 3 mm of copp For curve *F* obtained with the Friedrich chamber, however, it equally possible to pass a straight line or a slightly curved li through the points above 1 mm filtration. Likewise for curve obtained with the Glasser chamber, the points above 1.5 mm cou be joined by a straight or curved line, although the former is perha the better of the two. Straight lines are shown in both cases to illu trate a possible explanation for the absorption curves shown invari bly by Mutscheller, his curves usually having been obtained wi thimble chambers.

If now we measure the slopes of the curves, we find that *F* and have straight portions with slopes −6.80 and −6.28, respectivel The points marked *f* and *g* on the standard-absorption curve ha also these slopes of −6.80 and −6.28, respectively. Thus for given beam of X rays we apparently find an absorption coefficie which varies considerably according to the technique used in measu ing it. To attain uniformity the most logical consequence seems t discard the thimble chamber as a means for making precise measur ments; for, inasmuch as the open-air chamber is free from wall effec and is the accepted standard, it is apparently the best availab means for making absorption measurements of the general radiation

Where, in practice, a thimble chamber is used in making preci quality measurements, care should be taken to correct for the wa effect.

TABLE 2

Filter	Slope μ	True λ_e	Bracket λ_e		Equivalent filter	Duane λ_e	H. V. L. Cu
			μ	λ_e			
1	2	3	4	5	6	7	8
mm	cm^{-1}	Å	cm^{-1}	Å	*mm*	Å	*mm*
0.1							0.238
.2	25.5	0.256					
.25	22.8	.243					
.3	19.9	.230					.475
.4	17.5	.224				0.183	.56
.5	15.4	.207	28.0	0.262	0.15	.178	.62
.6	14.4	.202	16.6	.214	.45	.172	.68
.7	12.8	.192	13.8	.198	.6	.168	.73
.8	11.4	.184	12.2	.189	.7	.164	.79
.9	10.5	.178	11.3	.183	.8	.161	
1.0	9.86	.174	10.5	.178	.9	.158	.86
1.1	9.25	.170	9.6	.172	1.05		
1.2	8.64	.165	9.0	.168	1.15	.153	1.00
1.3	8.40	.163	8.5	.164	1.25		
1.4	7.94	.160	8.1	.161	1.37	.143	1.04
1.5			7.8	.158	1.45	.144	
1.6	7.53	.156					1.18
1.7			7.2	.153	1.8		
1.8	7.15	.153					
1.9			6.7	.148	1.9		
2.0	6.42	.146					
2.1			6.2	.144	2.1		
2.2	5.98	.142					
2.4	5.80	.140					
2.6	5.40	.136					
2.8	5.25	.134					

2. COMPARISON OF QUALITY MEASUREMENTS

Having reviewed the methods of making quality measurements, e shall now compare the results obtained by applying each method the same heterogeneous beam of X rays generated by a practically nstant potential source of voltage.

In order to better coordinate this comparison we shall refer all easurements of quality to those of the so-called true effective wave ngth without meaning to imply thereby that this method is prefer- le or necessarily the most correct. It is, however, less arbitrary an other methods.

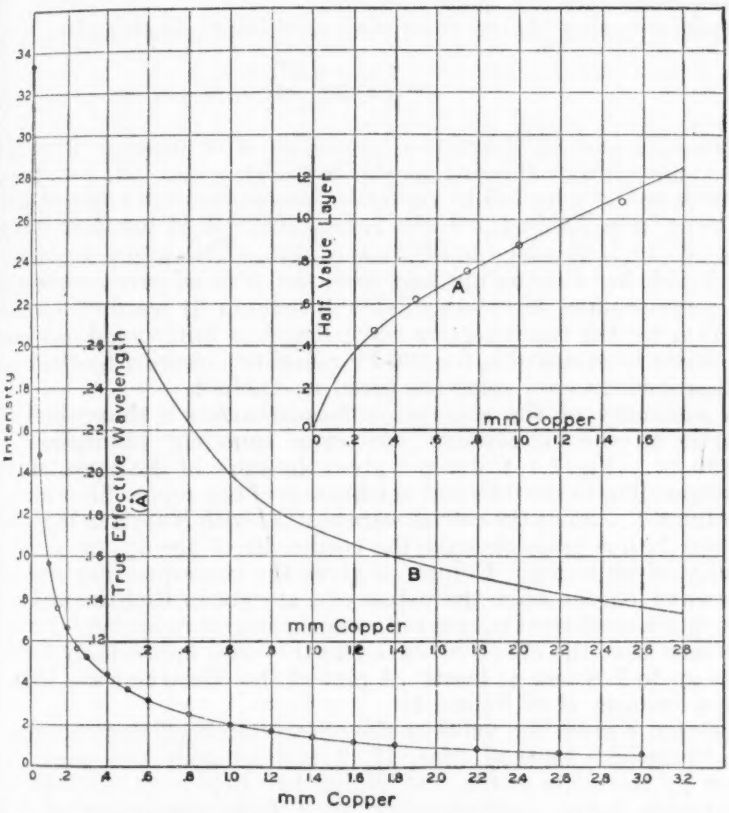

FIGURE 5.—*Curves showing half-value-layer and true effective wave length obtained from the same absorption curve*

Through the courtesy of Prof. H. Holthusen, of Hamburg, a family f curves was available, showing the relation between the half-value ayer in copper and the tube voltage (constant) for a series of filtered adiations. Half-value layers were obtained from each of his curves t points corresponding to 130 kv and plotted as circles in the H. V. L. urve. (Inset A in fig. 5.) The excellent agreement of our experi- ental results with Holthusen's shows the reliability of the H. V. L. ethod for constant potential, and gives further proof of the correct- ess of our above experimental procedure.

We may now make a simple comparison of the effective wave length obtained by the slope and bracket methods. For example, if we were to take as the absorption coefficient the slope of the line joining the two points a and b on the absorption curve (fig. 1), corresponding to filters of 0.5 and 1.5 mm of copper, this will give the slope corresponding to a filtration of 0.9 mm at the point c instead of at 1 mm. If the points 1 and 2 mm were chosen instead, the effective wave length would be much more nearly the correct value at 1.5 mm. For small filtrations the error in the bracket type of measurement is considerable. Above a certain filtration the method may be sufficiently accurate for many purposes. It has the advantage of requiring but two measurements

From equation (8) the absorption coefficient μ is given by

$$\mu=\frac{1}{x}\log_e\frac{(E')}{(E'')} \tag{10}$$

where (E') and (E'') are the intensities after passing through the two copper filters differing in thickness by x cm. If, for example, we wish to find μ for 133 kv radiation filtered through 1 mm of copper we have from Table 1, column 3, $\log_e(E')=2.44$ for filter 0.5, and $\log_e(E'')=1.43$ and for filter, 1.5 mm. This gives $\mu=10.1$ and $\lambda_e=0.174$ Å. Comparing this with the true effective wave length for 1 mm copper filtration (Table 4, column 3) we find a value of 0.169 Å for the true effective wave length, a fairly good agreement.

A series of values of λ_e for 130 kv radiation obtained by the bracket method (where $x=1$ mm) are given in Table 2.

A summary of the absorption measurements is shown in Table 2 wherein all the calculations are taken from the absorption curve at 130 kv. (Fig. 1.) Column 2 gives the slope of the curve at points corresponding to the different thicknesses of the copper filter indicated in column 1. Since the curves were plotted with Naperian logarithms column 2 thus gives directly the coefficient of absorption μ for each quality of radiation. Column 3 gives the corresponding true effective wave lengths when the values of μ are put in Richtmyer's copper absorption coefficient curves for monochromatic radiation. From this it is seen that the effective wave length varies appreciably for filtrations up to 2.8 mm at least. A plot of the effective wave lengths is shown in inset B of Figure 5.

Column 4 gives the value of the absorption coefficient obtained by the "bracket" method (Sec. II, 2 (a)) wherein the coefficient is given by the slope of the line joining two points on the logarithmic absorption curve, corresponding to a filter separation of 1 mm. The intermediate filtration of the two is that shown in column 1. Column 5 gives the effective wave lengths corresponding to the absorption coefficients of column 4, from which it is seen by comparison with column 3 that, as should be expected, the values approach the same limit for higher filtrations. Column 6 gives the approximate filter thickness on the true absorption curve for the effective wave lengths of column 5, thus indicating the divergence in terms of filter thickness. For example, consider a beam having an initial filtration of 0.6 mm copper. Its true effective wave length is 0.202 Å, whereas that derived by the "bracket" method is 0.214 Å and would correspond to a filtration of about 0.45 mm on the logarithmic absorption curve. Such a discrepancy shows a

nce that the bracket method, using a filter separation of 1 mm is ot satisfactory for obtaining effective wave lengths in close agreement with the true effective wave length except for higher filtrations.

Column 7 gives the effective wave lengths obtained by Duane's ethod, using a 1 mm filter separation, from which it is seen that he difference between λ_e, as obtained by the slope of the curve and s obtained by Duane's method, is large over the whole range of ltrations used. Applying the same measurements, however, we btain a fairly good measure of λ_e for the radiation corresponding the average filtration. Thus for 0.7 mm initial filtration, the rue effective wave length is 0.192 Å; by the 1 mm bracket method, 0.198 Å, whereas by Duane's (1 mm) method, 0.168 Å. When comaring Duane's effective wave length using 0.25 mm copper with the rue effective wave length, the differences are not large except for nfiltered or lightly filtered radiation.

From the practical standpoint we must not ignore the advantages f Duane's method. It requires but two intensity measurements ith given filters and reference to a predetermined calibration curve; t is sufficiently accurate for many of the present-day medical needs.

The half-value layers in copper for the same radiation are given n column 8 and it is seen that, throughout the entire length of the bsorption curve, these are decreasing continuously at least up to n initial filtration of 1.6 mm. The data of column 8 are plotted in nsert *A* of Figure 5. As pointed out in (II, 2 (*c*)) there can be no ixed relation between the half-value layer and effective wave length except for strictly constant-potential X rays. Curves showing the elation between the two have been given by Neeff and Reisner [34] nd others, under different conditions, but none lead to any coordiated relationship.

TABLE 3

Chamber	Filter	E/E_o	λ_e (Duane)	Percentage difference E/E_o	Percentage difference λ_e	λ_e calculated
1	2	3	4	5	6	7
	mm	*Per cent*				
S	0.25 Cu	17.7	0.37	22.4	8.1	0.368
F	.25 Cu	23.3	.34			.343
S	1.0 Cu	6.5	.26	30.9	7.5	.263
F	1.0 Cu	9.4	.24			.234
S	2.0 Al	41.8	.47	11.6	4.2	----------
F	2.0 Al	47.3	.45			----------
S	4.0 Al	27.4	.41	15.1	2.5	----------
F	4.0 Al	32.3	.40			----------

Table 3 shows the results of determining the effective wave length of the unfiltered radiation by Duane's method, using both a standard (*S*) and a thimble (*F*) ionization chamber for the intensity measurements. Column 1 indicates the type of chamber used; column 2 is the filter thickness used in the determination of λ_e; column 3 gives the percentage transmission of the respective filters for which are given the corresponding values of λ_e in column 4, obtained from Duane's curves for effective wave lengths.

[34] T. C. Neeff and A. Reisner, Strahlen., **32**, p. 190; 1929.

It is interesting to note for lightly filtered radiation, how dependent is the measurement of λ_e on the type of ionization chamber used. For example, in the first case λ_e differs by 8.1 per cent for the two chambers, while the respective percentage transmissions differ by 22.4 per cent (column 5). In order to check Duane's curves, λ_e was calculated using equations (2) and (3a), and the very good agreement is indicated in column 8.

If the quality of a beam of unfiltered radiation is desired, we are confronted by the question of which one of the eight values in Table 3 is to be used. Obviously no one of the methods will give a correct value of λ_e, nor can we readily obtain the slope of the absorption curve with any degree of accuracy at zero filter. We must thus choose an arbitrary techinque for making this measurement or else use some other method, such as the half-value layer in copper or aluminum. Here, again, it will be found that only a standard ionization chamber will give accurate and reproducible results.

TABLE 4

Chamber	Filter	True λ_e	Percentage difference, standard	Bracket λ_e	Percentage difference, bracket and same chamber	Percentage difference, standard	λ_e Duane	Percentage difference, Duane and same chamber	Percentage difference, standard
	1	2	3	4	5	6	7	8	9
Standard	0						0.37		
	.25	0.247		0.248	+0.4		.222	−11.3	
	.5	.207		.204	−1.5		.192	−7.8	
	.75	.185		.184	−.5		.177	−3.9	
	1.0	.169		.169	0		.167	−1.2	
Friedrich	0						.34		
	.25	.241	−2.4	.249	+3.2	+0.8	.222	−8.3	−11.3
	.5	.210	−1.4	.205	−2.4	−1.0	.190	−9.5	−8.9
	.75	.172	−7.0	.173	+.6	−6.5	.165	−4.2	−12.1
	1.0	.156	−7.7	.156	0	−7.6	.150	−3.9	−12.6
Glasser	0						.34		
	.25	.250	+1.2	.255	+2.0	+2.7	.224	−10.5	−10.5
	.3	.201	−4.5	.210	+4.5	+1.4	.193	−4.1	−7.4
	.75	.184	−.5	.185	+.5	0	.176	−4.3	−5.1
	1.0	.170	+.6	.170	0	+.6	.164	−3.5	−3.6

NOTE.—Groupings as follows: Columns 1, 2, and 3; columns 4, 5, and 6; columns 7, 8, and 9.

Table 4 gives a further comparison of the three methods of determining the effective wave length of 133 kv filtered radiation, using for each filter the standard Friedrich and Glasser ionization chambers. Column 1 gives the filtration of the beam; column 2, the "true effective wave length" obtained from the slope of the absorption curve; column 4, the effective wave length by the bracket method with a filter separation of 0.25 mm; and column 7, Duane's effective wave length, using a 0.25 mm copper filter.

Column 3 gives the percentage difference between the true effective wave lengths obtained with two thimble chambers and the values obtained with the standard chamber. It is evident that the disagreement is somewhat random, although the values obtained with the Glasser chamber appear to agree better with those of the standard.

Column 5 gives the percentage difference between the effective wave lengths obtained when using the slope and bracket methods with each of the three chambers. Here we see that when using the standard chamber the two methods agree very closely, whereas for the thimble chambers the agreement is considerably poorer. It is also seen that for high filtrations the two methods agree well within the experimental error.

Column 8 gives the percentage difference between Duane's and the true effective wave length as measured with the standard and thimble chambers. As expected from Section II the differences are large for all filtrations, although they become less for increasing filtration.

It must be emphasized again that, for much of the medical work done, the differences in effective wave lengths due to the use of thimble chambers is of no great importance. The fundamental difference between the three methods described is, however, of sufficient magnitude to be taken into consideration for all types of work.

Table 5 summarizes a series of absorption measurements made by Failla for the same radiation, but using six different types of ionization chamber. Columns 2 to 7 give the true effective wave lengths for the initial filtrations given in column 1.

From the discussion above we see that, while Duane's effective wave lengths are not the closest to the true effective wave length, they are the simplest to determine, requiring but one intensity measurement besides that of the original beam. The bracket method is considerably closer, but requires two extra intensity measurements. In both of these methods the accuracy of the measurement is very dependent upon the filter thickness, as stressed by Duane, who recommends the use of the mass per square centimeter of the filter instead of its thickness, the former being much easier to measure accurately. To obtain the "true effective wave length," of course, requires a series of intensity measurements, and consequently is not so applicable in practice as the other two methods.

TABLE 5

Filter	Standard λ_e	Drum λ_e	Bakelite λ_e	Graphite sphere λ_e	Aluminum mesh λ_e	Aluminum sphere λ_e
(1)	(2)	(3)	(4)	(5)	(6)	(7)
mm	*Å*	*Å*	*Å*	*Å*	*Å*	*Å*
0.25	0.256	0.244	0.261	0.246	0.247	0.264
.50	.192	.193	.187	.201	.185	.212
.75	.177	.177	.171	.178	.181	.192
1.00	.164	.165	.160	.166	.170	.179

For reference, curves are given showing λ_e as a function of the percentage transmission of the filter. (Fig. 6.) These are identical with Duane's curves and may be used in determining λ_e by his method. In applying these curves to the bracket method it must be clearly understood that the intensity measurements are made for filter thicknesses equally above and below the filter used in practice.

IV. RECOMMENDATIONS ON THE PROCEDURE FOR QUALITY EXPRESSION

In the foregoing discussion it has seen shown that a large numb of methods of quality expression have been proposed and used. F example, in the work of Burby and Barry, and Pohle and Barnes we find some half-dozen methods of determining the effective wa length, although the authors have carefully explained the use of ea method. Likewise, Quimby [36] used several kinds of λ_e in addition the absorption coefficient of the radiation to express quality—wi

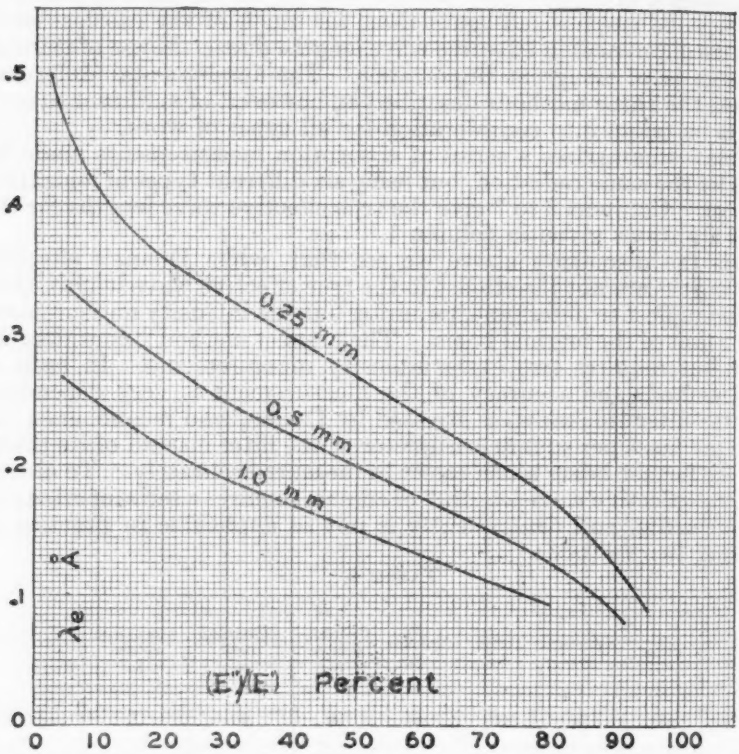

FIGURE 6.—*Effective wave length as a function of the percentage transmission through given filters of finite thickness*

proper explanation in each case. As shown in (III, 3, (b)), it i impossible to readily correlate effective wave lengths when obtaine with different filter thicknesses.

In all the methods for obtaining λ_e, two steps are involved— determining an absorption coefficient μ of the radiation by some mean and from this the wave length of monochromatic radiation having th same μ. For certain ranges Pohle and Barnes found that Duane' effective wave-length curves were inadequate, and consequentl expressed λ_e in terms of the percentage transmission of a given filter— a physically undesirable procedure. The fact remains that at presen

[35] See footnotes 4 and 6, p. 518.

[36] See footnote 5, p. 518.

the monochromatic wave length copper absorption coefficients have not been determined over the full range needed to determine λ_e for all the radiations used in X-ray therapy.

It seems reasonable, therefore, to recommend that the absorption coefficient in copper or aluminum of a heterogeneous beam of X rays be used alone to express the quality, stating the methods used in its determination. If desired at any future time, it is then a simple matter to express from available data the effective wave length in the ranges where possible. Such a method would, for example, eliminate any confusion in Pohle and Barnes' tables.

As shown in II, 1, the most accurate value of the composite absorption coefficient is obtained when using an infinitesimal filter thickness. The degree of agreement between this and one of the finite filter methods has been shown in Table 2.

In practice, μ may be determined (1) directly from the slope of the copper absorption curve, giving the true absorption coefficient; (2) by Duane's method, giving an approximate absorption coefficient; and (3) by the bracket method, giving a value in closer agreement with the true absorption coefficient. The first requires a series of measurements. The second and third require but two measurements and μ is calculated from equation (10).

For reference, Figure 7 gives curves for the absorption coefficient as a function of the percentage transmission of several thicknesses of filter which may be used in applying methods 2 and 3 above. These apply for a filter of any material but care must be taken that the material and thickness are always specified.

V. SPECTRAL ENERGY DISTRIBUTION AS DERIVED FROM COPPER ABSORPTION MEASUREMENTS

We may now turn to one other application of the foregoing copper absorption measurements, namely, the determination of a qualitative picture of the energy distribution in a beam of filtered heterogeneous radiation without the use of a spectrometer.

The effect on an X-ray beam of adding successive layers of a filtering material (copper for example) is to reduce the intensity of all incident wave lengths according to the absorption law expressed in equations (3) and (3a). As seen from this equation, the greatest absorption occurs in the longer wave lengths so that by increasing the filter thickness the energy becomes relatively more and more concentrated in the shorter, more penetrating wave lengths.

If, to take a particular case as an example, a tungsten target X-ray tube be operated below the critical voltage (70 kv) at which the characteristic K series of lines appear, the effect of increased filtration is such that the maximum of the spectral energy distribution curve of the filtered radiation shifts steadily toward shorter wave lengths. It would be expected that for such conditions a logarithmic plot would approach asymptotically a straight line, the slope of which is the μ for the short wave length limit. Since this would require that the remaining energy be practically zero, we would not expect the absorption curve to become straight for filtrations ordinarily used (0 to 3 mm copper).

However, in the case of operating the same tube well above its critical voltage; for example, at 150 to 200 kv, the K lines will be

present and conditions altered. The effect now of increased filtration is again to reduce the energy at all wave lengths, the resulting energy distribution being dependent upon the voltage and filtration; but in general, the energy transmitted through thick copper filters will consist of several practically monochromatic lines—the several K lines and the "end" radiation at the short wave length limit.

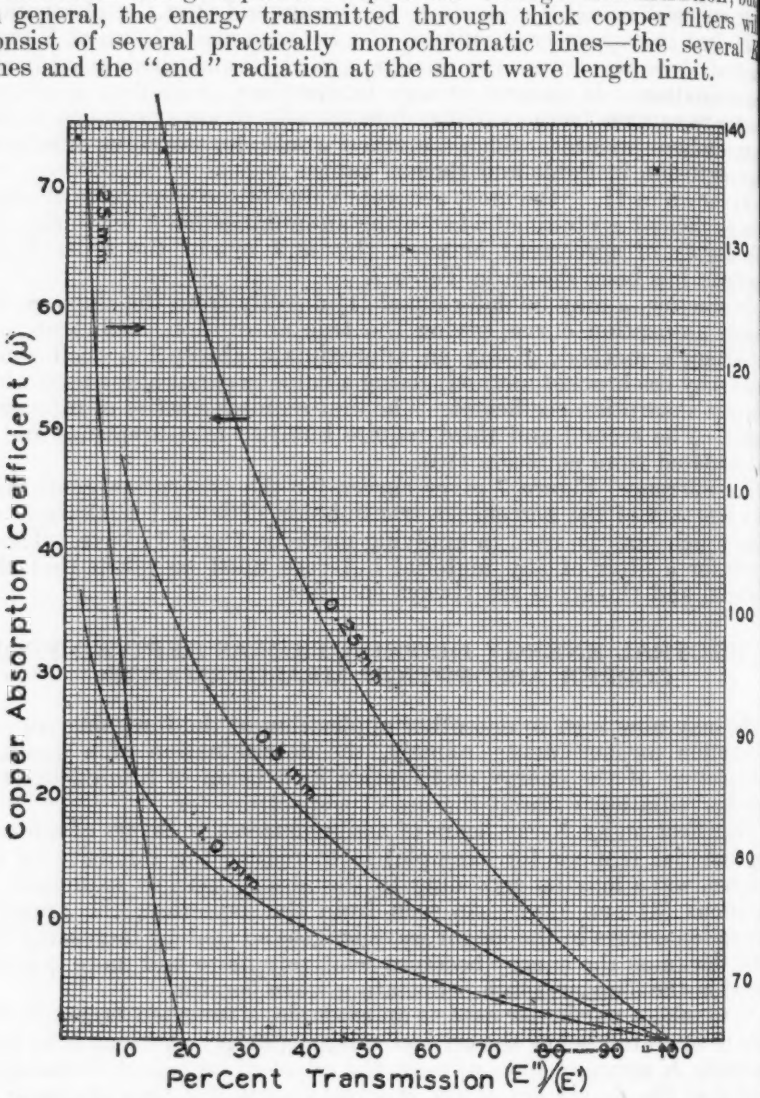

FIGURE 7.—*Copper absorption coefficients as a function of the percentage transmission through given filters of finite thickness*

Note that the curve for 0.25 mm filter is in two parts.

At present we have no very accurate data concerning the relative intensity of the K_α lines in comparison with the continuous spectrum background. There will always be present a certain amount of this radiation of shorter and less easily absorbed wave lengths, and it is thus impossible to state in advance the expected form of the logarithmic copper absorption curves for such radiation after high filtration

if the amount of continuous radiation were negligible, compared that of the line radiation, could it be expected that the absorp- curve would become straight, thus indicating a constant absorp- coefficient μ. At tube potentials of the order of 150 kv it has tacitly assumed by some workers that a large part of the spectral gy comes from the K_α lines of tungsten which appear at wave ths of about 0.2 Ångstroms, thus accounting for a straight end he absorption curve. However, such a distribution of energy, in highly filtered radiation, is contrary to experience.

aving obtained values of λ_e for copper filtrations up to 3 mm ee that the effective wave length of 130 kv radiation does not oach the wave lengths of the tungsten K_α lines which occur at t 0.208, 0.213, 0.184, and 0.179, Å, respectively. The nearest oach of λ_e to these wave lengths occurs for about 0.6 to 0.8 mm of per filter; whereas, for the maximum filtration used, λ_e was about 4 Å. This is a reasonable value of λ_e, since for the voltage used minimum wave length λ_o of the spectrum is 0.095 Å. The fact $\lambda_e = 0.134$ Å is nearer $\lambda_o = 0.095$ Å than the wave length of the nes gives further indication that the larger part of the energy pass- through the filter is not that of the K lines, but that of the contin- s spectrum background instead.

s a qualitative check of the above reasoning, we may refer to e approximate spectral energy distribution curves obtained by ne [37] with an ionization spectrometer. The curve shown was made 61 kv (constant potential) and 1 mm of copper, and it is shown eby that the greater part of the remaining energy apparently at shorter wave lengths than the first-order tungsten lines.

VI. SUMMARY

. A qualitative theory of copper absorption measurements shows t, for a known spectral energy distribution, an effective wave gth may be determined which is definitely related through known orption laws to that distribution.

. The logarithmic copper absorption curves for heterogeneous h voltage X-radiation do not become straight for filtrations up to m copper when the measurements are made with a standard ization chamber.

. Absorption measurements, applied to the problem of describing quality of a heterogeneous beam of X rays, show (*a*) that measure- nts of the so-called "average wave length" of the radiation have meaning as long as they are based strictly on the logarithmic orption curve becoming straight for filtrations greater than the omogeneity filter"; (*b*) the "half-value layer" method of express- quality is sensitive at least up to 1.6 mm copper filtration but is dily reproducible only for strictly constant voltage applied to the ay tube; (*c*) the most logical expression of the "effective wave gth" is obtained when using the absorption coefficient given by the pe of the logarithmic absorption curve. This is called the true ctive wave length.

W. Duane, Am. J. Roent., 9, p. 167; 1922.

4. Duane's method for obtaining the effective wave length gi values consistently lower than the true effective wave length, althou the difference is not great enough at higher filtrations to have s significance for most medical work. If this method is used the thi ness of copper used in the measurement should be stated.

5. The bracket method for determining the effective wave leng is more accurate than any other approximate method, but requir one more observation than the Duane method.

6. Absorption measurements made with the more common for of thimble ionization chamber are subject to error due to the chamb "wall effect." Such error is minimized in the true effective wav length method.

7. The absorption coefficient obtained with a standard thickness copper (or aluminum) is recommended as the simplest general meth of describing the quality of a heterogeneous beam of X rays for ther peutic uses. Due to a lack of monochromatic wave-length absor tion data over a sufficient range, it is impossible to extend the fective wave-length method over the whole range of radiations countered in X-ray therapy. Thus, for a perfectly general physi definition of quality, the "true" absorption coefficient obtained fr the slope of the absorption curve is recommended.

8. The effect on heterogeneous tungsten radiation of increasi the copper filtration is the concentration of the major part of t transmitted energy in wave lengths shorter than the K series of lin

Recognition is due G. Singer, of this laboratory, for having carri out the experimental part of this work.

WASHINGTON, December 1, 1929.

HANGE OF ELECTRICAL PROPERTIES OF RUBBER AND GUTTA-PERCHA DURING STORAGE UNDER WATER

By Harvey L. Curtis and Arnold H. Scott

ABSTRACT

A number of samples of rubber and gutta-percha were stored under water for out seven years and electrical measurements made on them periodically to termine the effect of aging on the resistivity, dielectric constant, and power tor. The dielectric constant was measured under three different conditions, mely, 60 cycles alternating current, pulsating direct current using 0.6 second arge with 0.1 second discharge, and pulsating direct current using the same time charge with 1 second discharge. In all cases the dielectric constants increased th time unless failure was approached. A sample was considered to have failed hen measurement of its capacitance became impracticable. The changes of the sistivity and power factor varied from sample to sample.

The approach of failure was first indicated by the resistivity. When a curve s plotted with time the sample had been under observation as abscissa and sistance of the samples as ordinates, the curves of the sample which failed showed break or marked change in direction several months before actual failure curred. With similar curves for power factor and direct-current dielectric con-ant, breaks occurred at a later time. The time interval between the break in e resistivity curve and the breaks in the other curves was a function of the rate decrease of the resistivity. These facts indicate that the failure of a sample is e result of its decrease in resistivity. This decrease in resistivity has been cribed to the formation of fine holes through the material. This explanation as confirmed by the microscopic examination of microtome sections of the mples which failed. These sections showed fern-like figures projecting into the bber.

All of the samples that failed were in the form of tubes, with water electrodes th inside and outside the tubes. Some copper salts were inadvertently allowed form inside the tubes. The catalytic action of these copper salts accelerated e aging, and probably changed its character.

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I. INTRODUCTION

The dielectric constant, power factor, and resistivity of a number f samples of rubber and gutta-percha which were stored under ater have been observed over a period of about seven years. During is time, measurements have been made on the average at two onths intervals.[1] These measurements showed marked changes in e values of all the specimens.

The changes which have been observed are doubtless the combined fect of oxidation, water absorption, and variations in temperature.

[1] On account of the pressure of other work some of the measurements have been discontinued and others ll be made at infrequent intervals. The results to date are presented in the hope that they may be of rvice to others who may be contemplating similar investigations.

As the specimens were always measured at room temperature, t temperature changes produced seasonal changes which can be large eliminated by drawing smooth curves when the data is plotted wi time as one coordinate. However, since water absorption increas with the amount of oxidation,[2] no attempt has been made to separa these two effects.

With some samples, the oxidation has been hastened by catalyt action of copper salts which were inadvertently present. On th account no conclusions can be drawn concerning the normal life these rubber compounds when stored under water.

II. DESCRIPTION OF SPECIMENS

Three classes of specimens were used in this investigation. The were 3 pairs of specimens from submarine cables insulated with rubb 11 specimens consisting of rubber tubes, and 4 specimens of gutt percha covered wire.

The cable specimens with rubber insulation were short lengt of submarine cables which were recovered during repairs to t Alaska cable system. Two pairs of specimens were taken from t cable which had been laid from Seattle to Sitka, while the third p probably came from the cable laid from Sitka to Valdez, Alask These six specimens are designated by the letter "A." The co position of the specimens taken from the Seattle-Sitka cable as r ported by the manufacturing company is given in Table 1. T other pair of specimens had a slightly different composition. A co plete analysis of the chemical composition of these specimens was n made. However, the ash determination showed that these specime contained more filler than the other cables. The rubber insulation these cable specimens was about 2.7 mm thick, and surrounded stranded copper wire about 2.5 mm in diameter. The specime were about 1,500 cm long.

TABLE 1

Specimen designation	Number of specimens	Form	Where obtained	Composition						
				Rubber	Paraffin	Whiting	Zinc oxide	Sulphur	Talc	
				Per cent	*Percent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Pe*
A-1	2	Cable	Seattle - Sitka submarine cable.	40.5			5.0	1.9	44.1	
A-2	2	do	do	40.5			5.0	1.9	44.1	
A-3	2	do	Sitka - Valdez submarine cable.							
T-1	4	Tube	Bureau of Standards rubber laboratory.	35.8	1.4		54.1	2.1		
T-2	2	do	do	40.0	1.4		48.9	2.4		
T-3	1	do	do	43.8	1.7		45.3	2.5		
T-4	1	do	do	43.5	1.5			2.2	47.1	
T-5	1	do	do	56.8	2.2			3.2	29.1	
T-6	2	do	do	40.6	1.7	16.6	32.4	2.1		
G-4	1	Cable	London			(a)				
G-5	1	do	do			(a)				

a Gutta-percha.

[2] Lowry and Kohman: The Mechanism of the Absorption of Water by Rubber, J. Phys., Chem., 31, p 1927.

The tube specimens were made in the rubber laboratory of the National Bureau of Standards, and they are designated by the letter "T." These tubes had a wall thickness of about 1.6 mm, an inside diameter of about 8 mm and lengths varying from 1,200 to 2,800 cm. They were quite varied in composition, but were not compounded according to any logical sequence. The exact compositions are given in Table 1. In general, the time of vulcanization was such as to give maximum tensile strength, but the time of vulcanization of one set was varied to show the effect of vulcanization on life.

The gutta-percha specimens were taken from samples of gutta-percha cables obtained from an English cable company, and presumably are all alike. They are designated by the letter "G." The diameter of the wire was about 1.6 mm, the thickness of the gutta-percha surrounding it was about 1.7 mm and the length of each specimen was about 3,000 cm.

III. CONDITION OF TEST

The outer electrode for each of these specimens was the water in which it was immersed. The inner electrodes for the rubber cable specimens and the gutta-percha specimens were the wires which the insulation covered. An inner electrode for each of the tube specimens was provided by passing a copper wire through the tube and then filling the tube with water. In these cases, then, the water was on both the outside and inside of the specimen.

The specimens were coiled into coils having a diameter of about 25 cm and placed in galvanized iron containers which were filled with water. The ends of the specimens were made to extend about 15 cm above the surface of the water in the containers. Guard electrodes were provided by wrapping strips of tinfoil around the specimens about 2 cm from the ends of the specimens.

The only care given the specimens was that of replacing the water that had evaporated. The mineral content of the water probably increased slowly with time because of the use of ordinary tap water for replacing the water which was lost by evaporation. No attempt was made to regulate the temperature, but records of the temperature at the time that measurements were made were carefully kept. The temperature varied from 13° to 26° C., the average winter temperature being 17° C. and the average summer temperature 25° C.

IV. ELECTRICAL MEASUREMENTS

The capacitance was measured by two different methods, one of which used direct current and one alternating current. Two separate measurements were made using the direct-current method known as the method of mixtures,[3] the difference in the two measurements being that the cycle of voltage application was different in the two cases. In both cases, the charging time was 0.6 second. During the first 0.5 second of this charging time, the condenser was mechanically connected to the charging battery, while during the last 0.1 second the condenser was insulated. In one case, the discharge time was 0.1 second; in the other case, it was 1.0 second. In this paper the capacitance obtained by these two methods will be

[3] H. L. Curtis, Mica Condensers as Standards of Capacity, B. S. Bul., 6, p. 441; 1910.

called the "tenth-second capacitance" and the "one-second capacitance." The effective dielectric constants computed from these capacitances will be correspondingly designated.

The effective dielectric constant is computed from the capacitance measured at a stated frequency. For other than perfect condensers the capacitance is a function of the frequency, and thus the effective dielectric constant is a function of the frequency.

The specimens were not made with sufficient exactness to permit an accurate determination of those dimensions which are required for computing the dielectric constant and resistivity of the materials. However, the same values were used in all the computations, so that the indicated changes are relatively correct. These relative changes were more important for this investigation than the absolute values.

The alternating-current capacitance and the power factor were measured at 60 cycles by means of a series inductance bridge.[4] In this paper the capacitance thus obtained will be called the "60-cycle capacitance" and the dielectric constant computed from this capacitance will be called the "60-cycle dielectric constant."

The resistance was measured by means of the direct deflection of a galvanometer.[5]

V. MICROTOME SECTIONS

Microtome sections were prepared of some of the specimens in order that they might be examined under a compound microscope. As it is impossible to cut thin sections of rubber at ordinary temperature, it was necessary to develop a special technique. The method used was a variation of the method used by Depew and Ruby.[6] It consisted of cooling the specimen to a temperature of approximately $-50°$ C., at which temperature it was sufficiently hard to permit the cutting of thin sections.

The specimen was held in the position for sectioning by freezing it to the top of a block which was clamped to the stage of the microtome. This block acted as a thermal insulator, so that the specimen could be cooled to the desired temperature without cooling the microtome. Firm bond between the specimen and the block was obtained by surrounding the specimen with water and freezing the water by means of a stream of cold air, which also served to cool the specimen.

The stream of air was cooled by means of liquid air. Air obtained from the regular compressed air line of the laboratory was passed through a drying tube to remove moisture and then carried to the bottom of a Dewar flask containing liquid air, so that it bubbled through the liquid, thus cooling to nearly $-180°$ C. Another tube leading from the stopper was directed so that the stream impinged on the specimen. The cooling of the specimen could be regulated by regulating the amount of air which passed through the Dewar flask. The arrangement can readily be understood from the diagram in Figure 1.

Since it was not feasible to measure the temperature of the specimen the correct temperature for cutting the specimen was a matter of judgment. If the specimen was too cold, it became so hard that it

[4] F. W. Grover, Simultaneous Measurements of the Capacity and Power Factor of Condensers, B. S. Bull., **3**, p. 371; 1907.

[5] H. L. Curtis and A. T. McPherson, B. S. Tech. Paper No. 299 (p. 679); 1925.

[6] Depew and Ruby, Some Microsections Cut from Vulcanized Rubber Articles, J. Ind. & Eng. Chem. **12**, p. 1156; 1920.

as brittle and also injured the microtome knife. If not sufficiently old, the specimen would give away from the knife and would not cut uniformly. As the cutting was necessarily done by a relatively warm knife, the cutting of the section tended to warm the specimen. Hence, after each cut the specimen was kept under the cold-air stream for several seconds in order to cool it to the necessary temperature for the next cutting.

The sections were permitted to reach room temperature before they were mounted in Canada balsam on a microscope slide after the method used for biological specimens. The most useful specimens had a thickness of from 5 to 10 μ. In examining the specimen a magnification of about 50 diameters gave the most useful information.

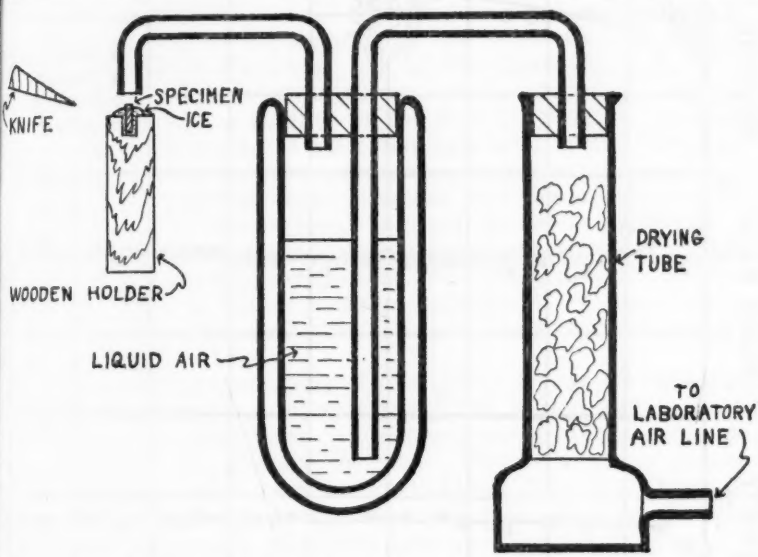

FIGURE 1.—*Diagram showing the method used to hold and cool rubber specimens for sectioning*

The specimen is cemented by ice to the top of a wooden block that is held in the clamp on the stage of a microtome. The ice is kept solid and the specimen cooled to the desired temperature by a stream of air which has been dried and passed through liquid air. The temperature of the specimen, which is regulated by the flow of air through the system, must be low enough so that the specimen will not yield under the pressure of the microtome knife and yet not be so low that the specimen is hard enough to injure the knife.

VI. RESULTS

On the basis of the results obtained from the electrical measurements, the specimens can be placed in four groups: (1) The rubber cables, (2) the tube specimens which have failed, (3) the tube specimens which have not yet failed, and (4) the gutta-percha covered wires. The complete data on only one specimen of each group are given, attention being called to any significant differences from the other samples of that group. The data are presented in the form of curves, the dielectric constants, power factor, and logarithm of the resistivity being plotted as functions of the time. The specimens which have failed are T–4, T–5, and the two specimens of T–6. The measurements were continued on these until further capacitance measurements could not be made with the equipment used, at which

time the material was considered to have failed. It might appear significant that the samples which failed contained either whiting or talc, but the specimens A–1, A–2, and A–3, not one of which has failed, also contained talc. It is impossible to compare the ageing qualities of these two types of specimens as the tube specimens were thinner than the cable specimens and their deterioration was accel-

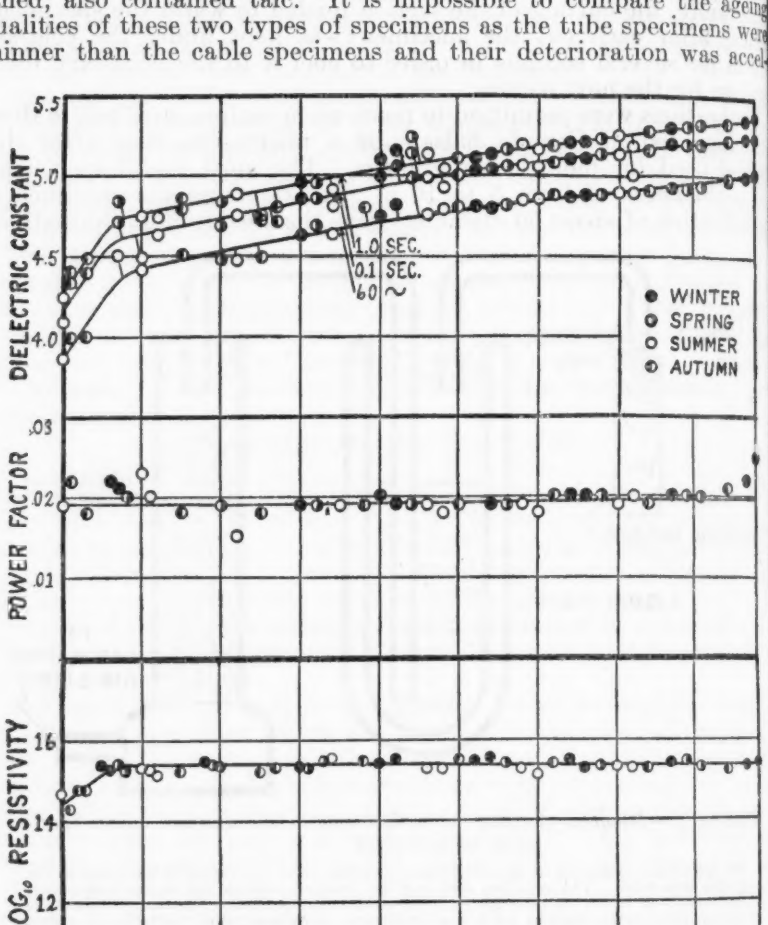

FIGURE 2.—*Changes of the dielectric constants, power factor, and resistivity of specimen A–1 with time stored under water*

This specimen was selected as typical of the group of submarine cables which did not fail during the 92 months under observation.

erated by the presence of copper salts. On the other hand, the cable specimens were in salt water at 4° C. for nearly 20 years before this investigation was started.

The results on A–1, which was selected from the group of rubber cables, are shown in Figure 2. The effective values of the dielectric constant as obtained by the methods already described are somewhat different at any one time, yet all of them increased at the rate

about 25 per cent in 92 months. The power factor did not show any change with time. The resistivity increased during the first five months, but after that there was no permanent change. However, there were large seasonal variations, as shown by the fact that the black dots (winter observations) are nearly all above the curve, while the open circles (summer observations) are below the curve. This was probably due to the change in temperature at the different seasons.

Of the five additional cables in this group, two gave results which are somewhat different from those of A–1. Instead of remaining constant, the power factors of these increased about 46 per cent, and the resistivities decreased about 75 per cent. However, the change in effective dielectric constant corresponded to that of A–1.

The changes with time of the electrical properties of sample T–1a, which was selected as an example of the tubes that have not yet failed, are shown in Figure 3. All of the three effective dielectric constants increased more than 50 per cent in 85 months, the major part of the increase occurring in the first 30 months. Moreover, with increasing time there is a decided separation of the three curves, the one-second dielectric constant having increased appreciably more than the tenth-second dielectric constant, and this in turn more than the 60-cycle. The power factor showed continuous increase from 0.021 to 0.048, together with very pronounced seasonal variations. The resistivity decreased for the first 30 months, then became nearly stationary. This indicates a closer correlation between resistivity and effective 60-cycle dielectric constant than between resistivity and power factor.

Of the remaining specimens of this group nearly all gave results which differed from those of specimen T–1a in one way or another. In two cases of the same composition, there was no change in the slopes of the curves of the effective dielectric constants, only a steady increase, and in one other case the power factor did not change permanently. The resistivity decreased in all cases, but in three cases there was no pronounced change in slope as was the case of specimen T–1a. There is no evidence that aging in any way depends on the vulcanization. The four specimens of T–1 each had a different vulcanization and there are no marked differences in the changes of the electrical properties of these with time.

The results on specimen T–4, which was one of the group of tube specimens that failed, are shown by the curves in Figure 4. Measurements were continued on this specimen for only 62 months, at which time the deterioration had become so pronounced that no satisfactory measurements could be made. During the first 54 months the effective dielectric constants had increased nearly 100 per cent, the three curves remaining approximately the same distance apart. The resistivity and power factor were constant until failure was approached.

The first indication that the specimen was approaching failure is found in the resistivity curve. At 44 months this curve bends sharply downward making a break in the curve. Ten months later the curves of the effective one-second and tenth-second dielectric constants turn toward the effective 60-cycle dielectric constant, making breaks in these curves. Four months after these breaks there appears to be a second break in the one-second dielectric constant curve when

the values which had been decreasing begin to increase. About t
time of the first break in the dielectric constant curves the pow
factor began to increase. However, even to the last measurement, t
effective 60-cycle dielectric constant curve showed no break.

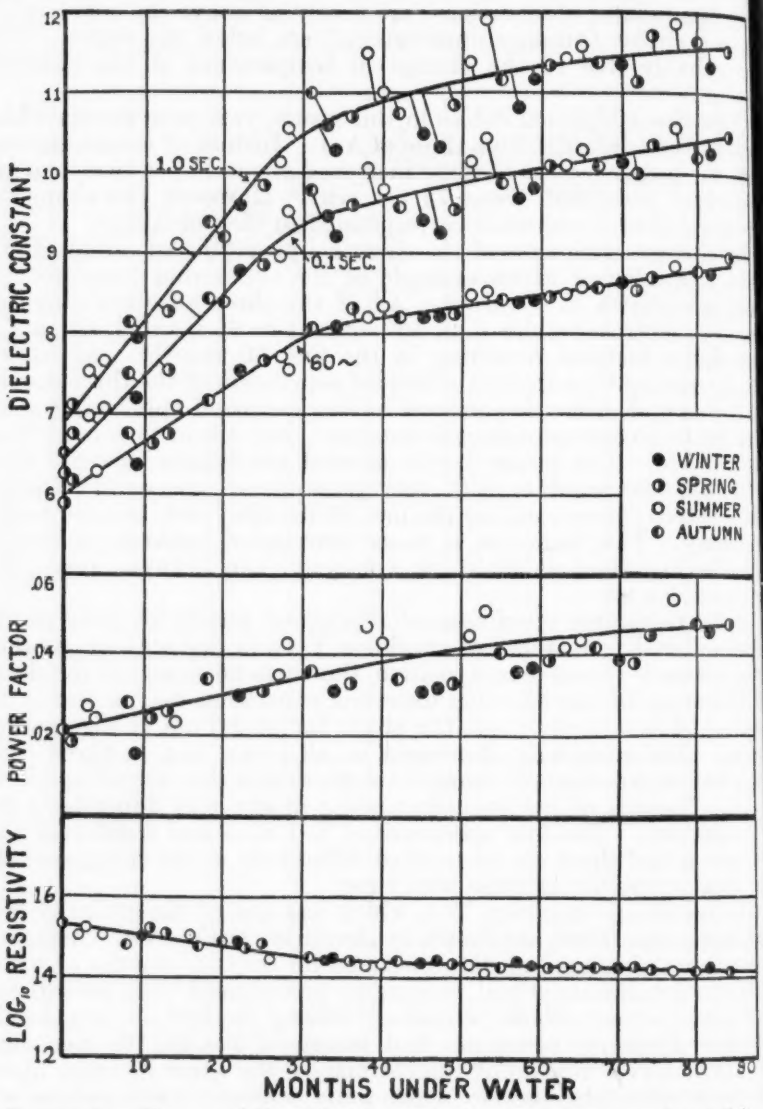

FIGURE 3.—*Changes of the dielectric constants, power factor, and resistivity of the specimen T–1a with time stored under water*

This specimen was selected as being typical of the group of rubber tubes which did not fail during the 85 months under observation.

The curves for the other three specimens of the group which failed were, in general, similar to the curves of T–4. The resistivity curves for the different specimens showed breaks at 66, 67, and 76 months. From 3 to 17 months after the breaks in resistivity curves, breaks

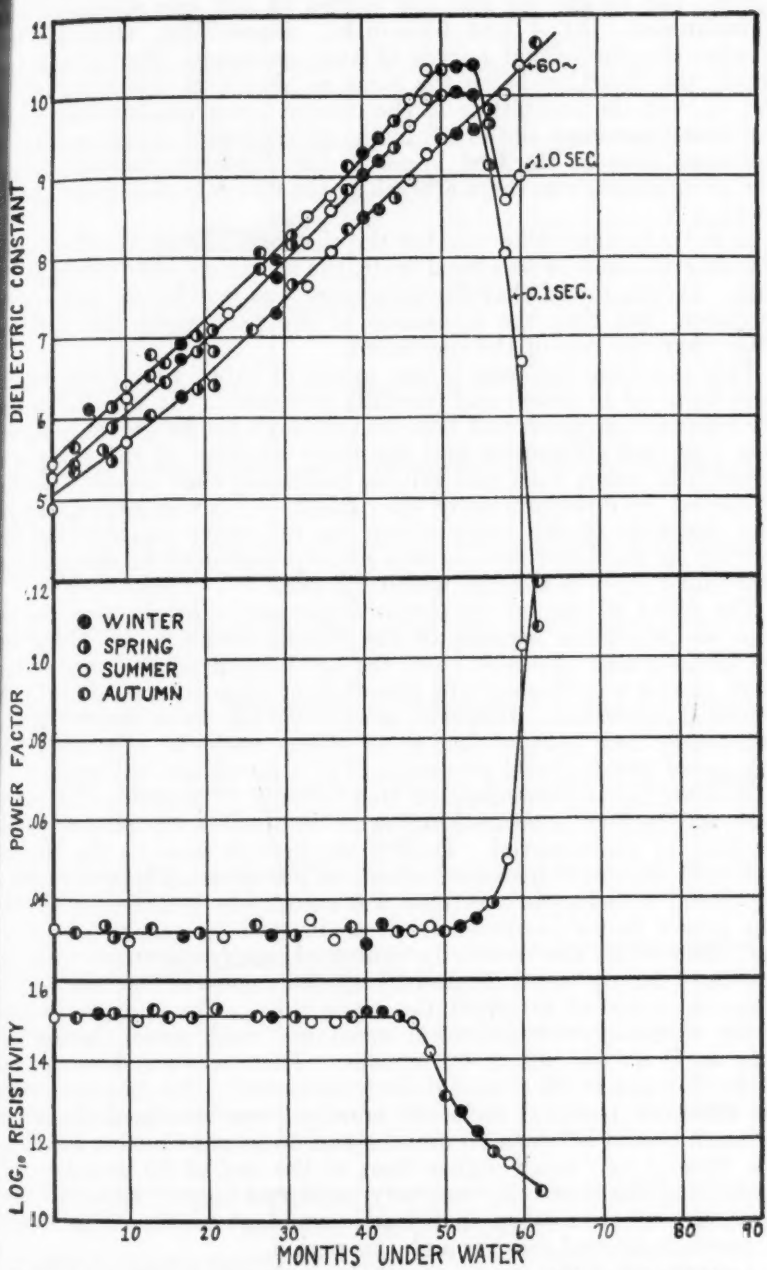

FIGURE 4.—*Changes of the dielectric constants, power factor, and resistivity of T–4 with time stored under water*

This specimen was selected as being typical of the group of rubber tubes which failed.

occurred in the one-second and tenth-second dielectric consta curves, the breaks for the two curves of any one specimen bei simultaneous. At 4 and 6 months, respectively, after the fir breaks, the one-second curves of two specimens showed a secon break, the direction being the same as shown in the curve of T- (fig. 4), but the magnitude of the change being considerably large For every specimen the break in the power-factor curve occurred a the same time as the first break in the dielectric constant curve For no specimen was there a break in the 60-cycle dielectric consta curve.

In order to determine whether the electrical failure was due to ge eral deterioration or to a local fault, the specimen was tested part b part. It was found that the resistance was low for all parts of th specimen, but that the resistance of the parts near the ends wa lower than the rest of the specimens.

This specimen and one of the group of tubes which did not fa were then cut to pieces and carefully examined. It was found tha the copper wire which had been run through the length of the speci men was badly corroded and the inner surfaces of the tubes wer greenish in color, hard and brittle, indicating that copper salts ha promoted the deterioration of the rubber. This was more noticeabl near the ends of the tubes where the resistance was lowest. Th coating on the inner surface was more pronounced in the specime that failed than in the one which did not.

The effect of age on the electrical properties of gutta-percha wa hard to determine because of the strong tendency for the gutta percha to crack. In most cases the crack occurred so suddenly tha there was no way of observing the effect of approaching failure on th electrical properties. However, in one case the crack developed at a sufficiently slow rate so that these effects could be observed. The changes of the electrical properties of G–4 are shown in Figure 5.

Measurements were made on G–4 for only 71 months, after which time satisfactory measurements were impossible on account of the cracking of the material. During the first 60 months the effective dielectric constants increased about 44 per cent. The separation of the effective dielectric constants was small, but increased with time. The power factor increased from about 0.01 to nearly 0.04 during that time while the resistivity remained nearly constant. The ap proach of failure was indicated by all the curves except the 60-cycle dielectric constant at about the same time. The changes in resis tivity, direct-current dielectric constants, and power factor were very rapid at the end of 60 months. There was a sudden decrease of the effective tenth-second dielectric constant. No measurement of the effective 1-second dielectric constant was obtained during the 6-month period between 60 months and 66 months but at the end of this time it was much higher than at the end of 60 months. The decrease of the resistivity was very rapid and large. As in the other cases, the effective 60-cycle dielectric constant continued to increase at about its normal rate through this period.

A summary of the results on all the specimens is given in Table 2. Only the 60-cycle dielectric constants are given. The percentage increases with time are about the same for the effective "tenth-sec ond" and "one-second" dielectric constants as for the 60-cycle, though in every case the latter was lower than the tenth-second con-

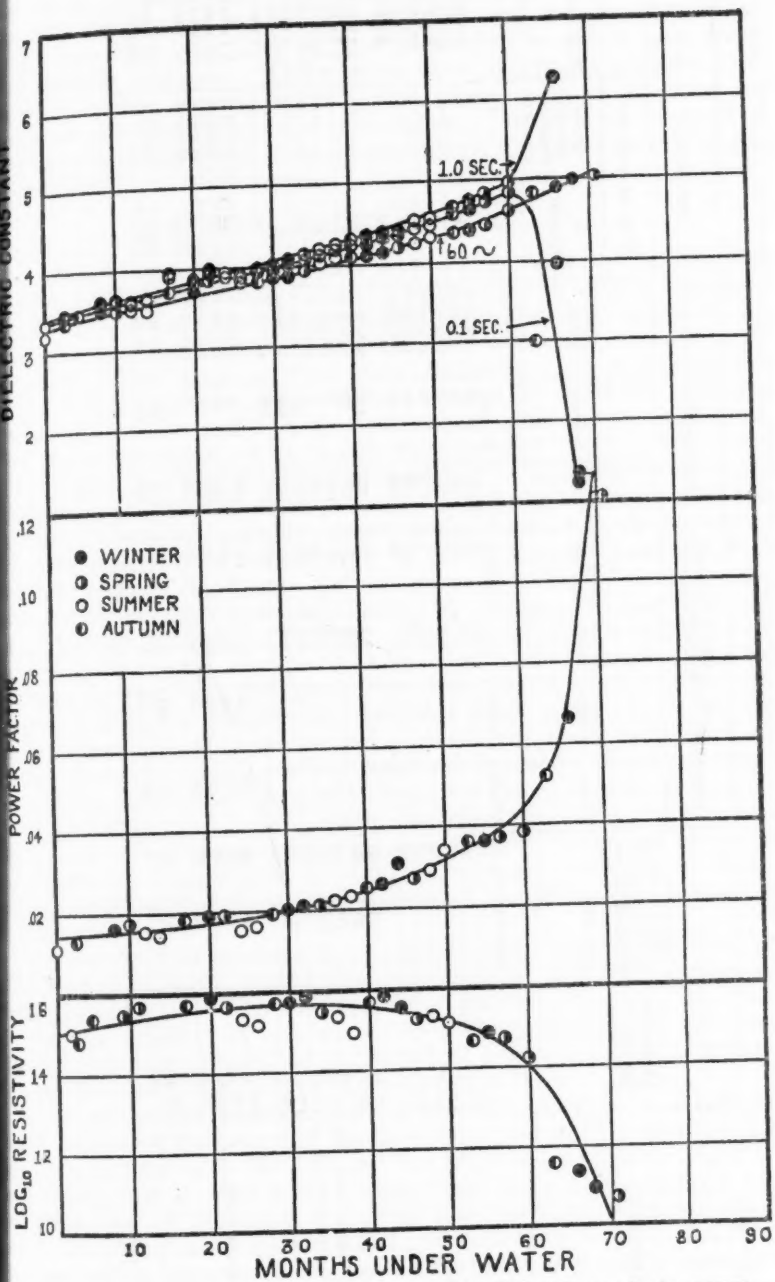

FIGURE 5.—*Curves showing the changes of the dielectric constants, power factor and resistivity of G–4 with time stored under water*

This specimen was one of the gutta-percha specimens, all of which failed.

TABLE 2

Type of specimen	Laboratory designation of specimen	Time of vulcanization at 40-pound steam pressure	Time under observation	Time to break of—		Effective 60-cycle dielectric constant		Power factor		Resistivity			
											Value at break of—		
				Resistivity	Dielectric constant	Initial value	Observed increase	Initial value	Observed increase	Initial value	Resistivity	Direct current dielectric constant	Final value
		Minutes	*Months*	*Months*	*Months*		*Per cent*		*Per cent*				
Submarine cable	A–1		92			4.0	25	0.020	20	5×10^{14}			20×10^{14}
	A–1′		92			4.0	25	.020	20	5×10^{14}			20×10^{14}
	A–2		87			4.4	7	.017	9	18×10^{14}			21×10^{14}
	A–2′		87			4.2	7	.017	9	18×10^{14}			19×10^{14}
	A–3		87			7.0	21	.026	46	15×10^{14}			5×10^{14}
	A–3′		87			6.9	28	.026	46	12×10^{14}			3×10^{14}
Tube specimens which have not failed	T–1a	15	85			5.9	53	.021	130	20×10^{14}			1.5×10^{14}
	T–1b	30	85			6.8	28	.029	60	16×10^{14}			1.0×10^{14}
	T–1c	60	85			7.6	40	.041	0	20×10^{14}			1.5×10^{14}
	T–1d	120	85			7.9	50	.047	9	17×10^{14}			0.05×10^{14}
	T–2	15	85			5.5	70	.017	100	15×10^{14}			2×10^{14}
	T–2′	15	85			6.1	41	.020	100	17×10^{14}			2.3×10^{14}
	T–3	15	81			4.7	79	.010	100	12×10^{14}			3×10^{14}
Tube specimens which failed	T–4	30	62	44	54	4.8	120	.033	4	12×10^{14}	12×10^{14}	0.57×10^{12}	5.5×10^{10}
	T–5	30	81	66	69	5.2	100	.033	12	12×10^{14}	13×10^{14}	$.12\times10^{12}$	3.7×10^{10}
	T–6	40	87	67	84	6.7	70	.026	0	11×10^{14}	1.9×10^{14}	$.18\times10^{12}$	18×10^{10}
	T–6′	40	87	76	79	5.9	68	.026	0	10×10^{14}	3×10^{14}	$.11\times10^{12}$	8.7×10^{10}
Gutta-percha	G–4		71	60	60	3.2	56	.011	250	9×10^{14}	1.6×10^{14}	$.64\times10^{12}$	5.5×10^{10}
	G–5		71	68		3.2	52	.012	250	9×10^{14}	$.1\times10^{14}$		140×10^{10}

ant, which in turn was lower than the one-second value. There s a wide variation of the percentage increase of the effective dielec- ic constant from specimen to specimen, but in every case there as a definite increase. There were even larger differences with ard to change of the power factor, some samples showing no preciable permanent change with time. The resistivity showed permanent change with time in two cases, increased in two cases, d decreased in all other cases.

VII. DISCUSSIONS OF RESULTS

The different speciments showed such a wide variation in behavior at very few general conclusions can be drawn. However, the data every specimen under observation show that the effective 60- le dielectric constant increased with time as long as measurements re made. This assumes that the dimensions have remained un- nged. Whether this increase was caused by chemical changes water absorption can not be determined from the present data. For those specimens which failed, the approach of failure was first icated by a marked decrease in resistivity. The observed breaks ich occurred in the effective one-second and tenth-second dielectric nstant curves were probably caused by the decrease in the resistance the specimen. The capacitance of the specimen measured with o-tenth second discharge always showed a decrease when the istance of the specimen fell below 10^{12} ohms, as shown in the xt to the last column in Table 2. The capacitance measured with e-second discharge always showed a decided change when the istance decreased to 10^{12} ohms, but this change was sometimes an rease, sometimes a decrease. In most cases, where there was an itial decrease of the one-second capacitance there was later an rease when the resistance had fallen sufficiently low. Apparently s peculiar behavior is brought about by the dielectric absorption the specimen, but no quantitative relationship has been estab- hed. This decrease and later increase is indicated in the curve for e one-second capacitance of Figure 4, though the increase in this e is so small as to have passed unnoticed had it not been for results other specimens.

The time interval between the breaks in the resistivity and dielec- e constant curves is seen to be dependent on the rate of decrease the resistivity. When the resistivity decreased rapidly this time terval was small. In the case of G–4 this interval was less than t between measurements and, therefore, from the curves it appears t the breaks in both sets of curves came at the same time.

The break in the power-factor curves can likewise be attributed the decreased resistance of the specimen, and in this case the rela- n is quantitative. So long as the resistance remains high the wer loss, due to conduction through the insulating material, is a gligible part of the total, but after the break in the power-factor rves, the loss due to the decreased resistivity accounts for the sharp rease which occurs in the power factor. A possible exception curs when the resistivity becomes very low, but under this condition easurements of both resistance and power factor are very inaccurate. Since all the changes in the observed curves as the specimen proached failure can be explained by the decrease in resistance, it pears that the direct measurement of the resistance is the best

method of determining the electrical failure of materials of this kin
This is emphasized by the fact that the break in the resistivity cur
occurs several months in advance of the break in any other curve.

The decrease in resistance of those rubber specimens which fail
is not caused by a single large hole opening through the insulatio
as was shown by the measurements on one of the tube specimen
where the resistance of all parts was low. An explanation whi
seems to fit the facts can be made by assuming that numerous fi
holes, which become filled with water, extend through or near
through the insulation. The resistivity of water is less than on
trillionth part of that of rubber so that a very few minute holes wi
explain the decrease in resistance. At the same time the measure
dielectric constant would not be appreciably affected by these hole
since the dielectric constant of water is never more than 30 times th
of the rubber. Little is known about the power factor of water, bu
apparently the observed break in the power factor curve is not incon
sistent with the above explanation of the cause of failure. Whil
this explanation fits the facts, there may be others which would b
equally satisfactory.

The above explanation has been confirmed by observations o
microtome sections of the failed specimens. A characteristic micro
photograph of a section is shown in Figure 6. Dark, fernlike figure
can be seen extending into the rubber from the surface on the inside
of the tube, many for at least one-third of the thickness of the rubber
While none has been observed which reaches entirely through th
rubber, this is no reflection on the above theory. The chances o
observing one are exceedingly small because few are required t
account for the observed resistivities and the portion of the specime
represented by the sections on the slides is minute.

Since this type of deterioration occurred only where copper salt
were present on the surface, it is probable that these salts have com
bined with the sulphur of the rubber to form cuprous sulphide, whic
has the dark color observed in the fernlike portions. Since copper
salts were present on all samples which were observed until failur
occurred, the conclusion concerning the change of electrical properties
in the approach of failure may not apply to samples where such salt
are not present. However, in a cable submerged in sea water, an
insignificantly small penetration of water through an exceedingly
small pore might start the formation of copper salts which would
rapidly enlarge the hole and cause a failure of the cable.

In some cases there was considerable change of the electrical prop
erties with the season, which probably was due to the change in tem
perature. This did not show up in the same property in all speci
mens. In the rubber cables the resistivity varied considerably with
the season, while the other properties did not vary so much. In the
tube specimens, the resistivity did not change much with the season
while the other properties did change. If the temperature had been
controlled, better determination of the effect of time on the electrical
properties would have resulted.

The authors wish to acknowledge the assistance of a number of their
coworkers at the Bureau of Standards. In particular, the specimens
for this investigation were made under the direction of S. Collier, and
the early electrical measurements were made by Miss Johanna Busse.

WASHINGTON, February 25, 1930.

FIGURE 6.—*Microphotograph of a section of specimen T–4*

This microphotograph of a section of a tube specimen which failed shows the dark fern-like figures extending into the rubber. These figures are probably caused by the presence of cuprous sulphide.

THE RESISTANCE OF STEELS TO ABRASION BY SAND

By Samuel J. Rosenberg

ABSTRACT

A study has been made of the adaptability of three types of apparatus, namely, the ball-mill, the sand blast, and the Brinell machine, to the testing of the resistance of metals to abrasion. A detailed description of all apparatus used is given.

The ball mill was generally unsatisfactory; the sand blast gave consistent results but did not differentiate between the materials tested, apparently because of the fact that the abrading conditions were not sufficiently severe; but the Brinell machine proved to be generally satisfactory.

The Brinell test showed that the resistance to wear of normalized, annealed, hardened, or tempered carbon steels increases with their hardness. Increasing the temperature of annealing resulted in a slight increase in resistance to wear, the increase being more marked in a low-carbon than in a high-carbon steel.

Abrasion in this type of test is caused by the gradual breaking up of the individual grains and not by the removal of separate grains in their entirety, and this action is accompanied by local strain hardening.

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I. INTRODUCTION

The problem of testing the resistance of metals to wear is one of the most perplexing problems confronting the testing engineer to-day. So many different variables enter, that it is generally agreed there is no universal test for determining the resistance of metals to wear. Attempts have been made, therefore, by various investigators, to study certain types of wear with machines especially designed to

simulate particular conditions of service, and this method seems to be the most promising mode of attack.

The object of this investigation was not to find a universal testing machine for all conditions of service, because the development of such a machine does not appear to be probable, but it was believed that closely controlled laboratory tests with a series of ferrous metals would be of value as a contribution to the general problem of the testing of the resistance of metals to abrasion.

Wear may be divided into two major types—wear caused by abrasion of metal on metal, and wear caused by abrasives on metal. The latter type only will be considered in this paper.

II. PREVIOUS INVESTIGATIONS

Probably the earliest work on abrasive wear was carried out by Robin.[1] His tests consisted in determining the wear of steels when rubbed under a known pressure on papers which were covered with an abrasive powder. A cylindrical steel specimen (50 mm in diameter) described a circular path having a diameter of 150 mm; the pressure used was 1 kg/cm^2, and the speed was 70 revolutions per minute. The abrasion number was the sum of the weights of metal lost by abrasion in three consecutive tests, each lasting a minute.

For the same type of steel with the same abrasive, two sheets of different papers gave comparable results. Precision was from 2 to 10 per cent on ordinary steel and from 15 to 20 per cent for very hard steels. The effect of variables was stated to be as follows:

Pressure.—Augments the wear approximately proportionately if within 0.5 to 2 kg/cm^2. In hard steels the wear increases at a more rapid rate and the curve is parabolic. The wear is proportional to the surface area of the specimen.

Speed.—Increases the abrasive power of the paper. Some steels are more sensitive than others, especially those which were also sensitive to variations in pressure.

Nature of abrasive.—Different abrasive materials and papers of different sizes of grain class the metals in approximately the same order while they give different figures as functions of the abrasive power.

Wear of steels.—In the case of annealed carbon steels, the wear is not proportional to the pearlite. A maximum of abrasion was found with 0.4 per cent carbon; in hypereutectoid steels the wear was approximately proportional to the carbon percentage. Increased fineness of the particles, cold work, and the presence of phosphorus increase the resistance to abrasion; the presence of silicon and manganese diminish it frequently. In cast metals the resistance grows with the phosphorus contents and with the percentage of iron carbide. The hardened steels can hardly be distinguished by this process; on the contrary, tempered steels lend themselves to this examination without any difficulty. The best resistance in hardened steels seems to be characteristic of the finest martensites.

The practical conclusions to be drawn for the domain of the science of testing are the following: Each mode of measurement and each kind of test leads to a special classification of the steels. The diverse modes of determining the wear can not be estimated by one and the same test. The test which has been explained so far appears only to lend itself for the examination of rails under certain special service conditions, to files, and to apparatus for disintegration, etc.

Brinell[2] tested a variety of materials for resistance to wear using a machine designed by him and described elsewhere in this report. The effect of variables was stated to be as follows:

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[1] Felix Robin, The Wear of Steels With Abrasives, Carnegie Scholarship Memoirs, Iron & Steel Inst., **2**, p. 6; 1910. Also Abrasion Tests of Steel, Internat. Assoc. Test. Mats., Sixth Congress, III$_6$; 1912.

[2] J. A. Brinell, An Investigation of the Resistance of Iron, Steel, and of Some Other Materials to Wear, Jernkontorets Annaler; 1921. A more convenient reference is the transcript, by H. A. Holz, Brinell's Researches on the Resistance of Iron, Steel, and Some Other Materials to Wear, Testing, **1**, p. 104; 1924.

1. Coarse-grained sand produces greater wear than finer sand under equal conditions.
2. In using pure quartz sand, wear is greater than that produced by ordinary sand.
3. Majority grain size of sand is of decisive influence as to abrasive action, therefore, two sorts of sand with equal size of smallest and largest grain may possess a widely different abrasive effect.
4. Grain form is not of influence, at least at pressures up to 10 kg, but in the investigation of softer materials at lower pressures the sand with sharp corners produces a greater wear than sand of round grain.

In the carbon steels he found that resistance to wear increased with hardness.

A machine for the determination of abrasive wear was described by Parker.[3] In making a test, the specimen was clamped with a definite force for a definite length of time against the face of an alundum grinding wheel, which was continuously dressed. The number of revolutions required to produce a given depth of wear was recorded automatically. The only results reported showed that of 3 materials, 1 untreated, 1 with a thin carburized case, and 1 with a thick carburized case, the last mentioned had the greatest resistance to wear, with the thin carburized case running a close second. The untreated material had a relatively low resistance.

A machine for determination of wear under wet grinding conditions was described by Blake.[4] In principle, the machine was an accurately controlled grinding machine in which all conditions as to abrasive, pressure, speed, time, and moisture were under control. The wear was measured by the amount of metal worn off in approximately 15,000 feet of travel at a speed of 125 feet per minute, with a pressure of 50 lbs./in.^{2} on a testing face of approximately 3 square inches, and the wear was expressed as the ratio of loss of weight of the metal tested to loss of weight of an adopted standard (commercially pure iron). His conclusions are:

> This abrasion tester has shown that each abrasive or mineral substance develops its own order of relative abrasion resistance for metals and that the position of any steel or alloy on a listing of abrasion factors will depend upon the nature of abrasive employed. In extreme cases it has been found that steels at the top of the list with one abrasive are at the bottom of the list with another. This discovery has eliminated the idea of securing general all-around high abrasion resistance in any one steel.

An actual service test was made by Clapp and Deveraux[5] in which six 5-inch diameter chromium steel balls and six 5-inch diameter chromium-molybdenum steel balls were placed in a ball mill. The material ground was 3-inch maximum size chalcopyritic ore in which the gangue was a hard shale and quartz. After six weeks the chromium steel balls were 2 to 2½ inches in diameter while the others were 4 to 4½ inches in diameter.

III. EQUIPMENT AND TEST METHODS

1. BALL-MILL TEST

The mill used for this test consisted of two cylindrical containers which revolved about their longitudinal axes during test at a speed of 55 r. p. m. The interior of the container used in the tests (only

[3] W. H. Parker, The Wearing Qualities of Tire Chains, Proc. Am. Soc. Test. Matls., **28–2**, p. 332; 1928.
[4] J. M. Blake, Wear Testing of Various Types of Steels, Proc. Am. Soc. Test. Matls., **28–2**, p. 341; 1928.
[5] E. C. Clapp and F. C. Deveraux, Tests with Molybdenum Steel Balls at Matahambre, Cuba, Eng. & Min. J. Press, **120**, p. 891; 1925.

one container was used) was lined with rubber to prevent the impinging of the steel specimens upon the porcelain walls. After being so lined, the size of the container was 9 inches in diameter by 12 inches long. Figure 1 shows a photograph of the apparatus.

The specimens used for this test were ground and lapped into 1-inch spheres. Ten kilograms of a certain sand was placed in the mill at the beginning of each test run, the samples were then laid in the sand, the cover tightened, and the mill started. Entirely new sand was used for each test. The diameters of the specimens were carefully measured and the losses of weight determined after each run. Wear was expressed as loss of weight (milligrams) per square centimeter of surface per hour of test.

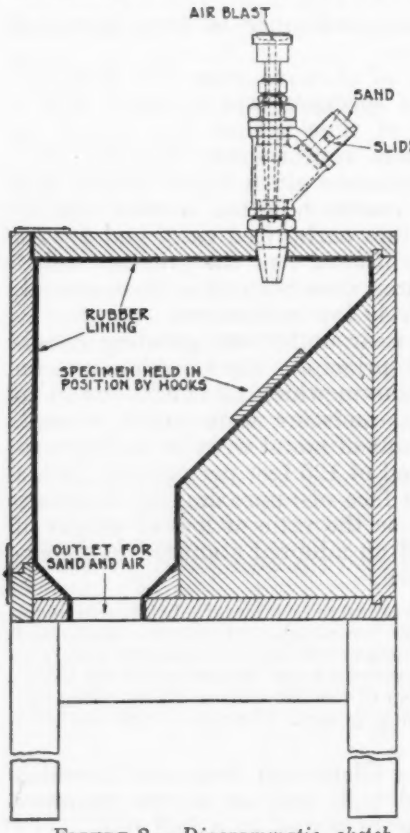

FIGURE 2.—*Diagrammatic sketch of sand-blast apparatus*

2. SAND-BLAST TEST

Since the sand blast is such a rapidly abrading process, it seems logical to attempt to adapt it to abrasion testing. Figure 2 is a diagrammatic sketch of the apparatus designed and used for this test. In this test a special nozzle, five-sixteenths inch in diameter, was placed in the top of a rubber-lined wooden box. The nozzle was connected to the bottom of a Y pipe fitting. Sand and air were introduced through the two upper branches of the Y, the air passing through an inner tube into the Y. The lower end of this tube, which carried the air blast into the nozzle, was below the point at which the sand was introduced so as to avoid "backing up" of the sand. The introduction of the sand was controlled by a slide valve.

The specimens used were flat, 3-inch squares, about one-fourth inch thick, held in place at an angle of 45° to the axis of the nozzle and about 3½ inches below it. An opening in the bottom of the box provided an outlet for the sand and air.

In all tests a weighed amount of sand was placed in the sand container. A rubber hose connected the bottom of this container with the sand inlet. The air blast was adjusted to the proper pressure, and a slide valve in the sand inlet was opened, thus giving an immediate and full flow of sand. The air blast, emerging from the tube,

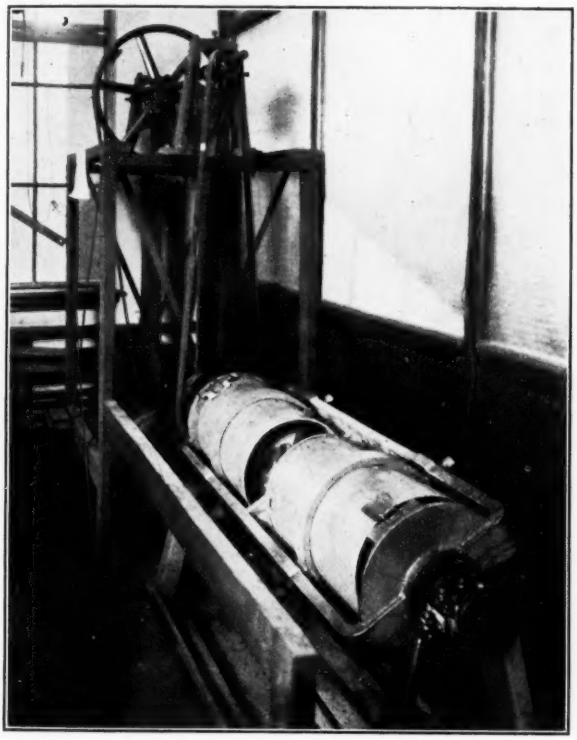

FIGURE 1.—*Ball mill*

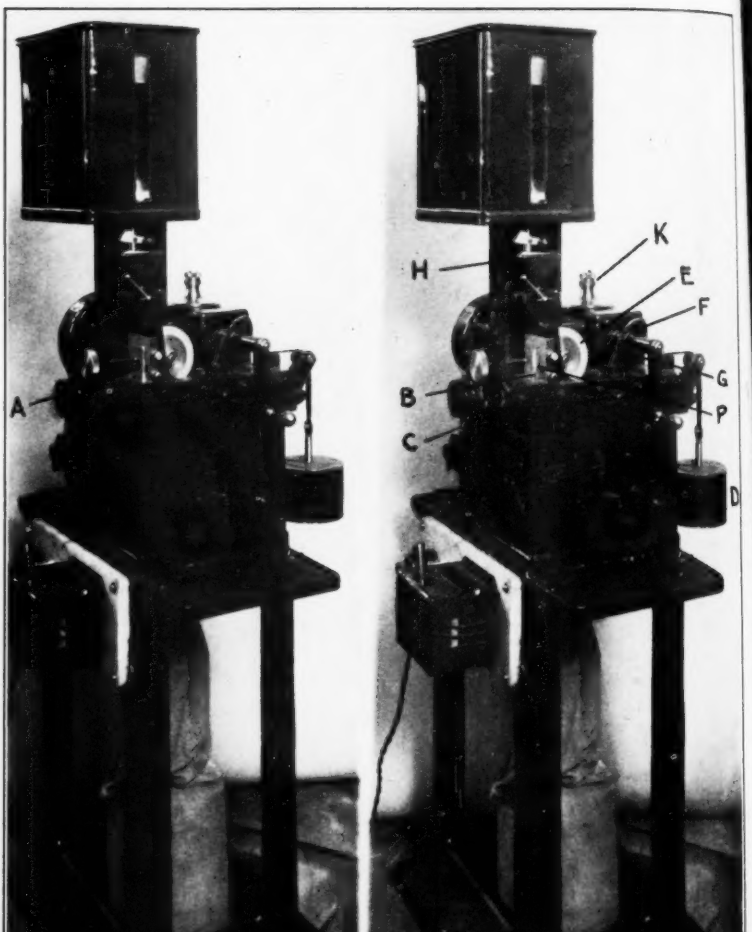

FIGURE 3.—*Brinell machine*

a, With specimen in position for test; *b*, with specimen removed.

...ped suck the sand downward and automatically caused mixture in ...e nozzle and abrasion of the specimen.

The specimens were cleaned and weighed before and after test, and ...e loss of weight taken as a measure of the resistance to wear. Sev...l consecutive tests were made on each specimen until a definite ...te of wear was observed.

3. BRINELL TEST

A photograph of the Brinell machine for testing the resistance of ...aterials to wear, with and without a specimen in place, is shown in ...igures 3 (*a*) and (*b*). In oper...ing the machine, the specimen, ..., was clamped to a slotted plate, ..., mounted on a carriage, *C*, to ...hich was attached a cord passing ...er a pulley and carrying the ...eights, *D*. A disk, *E*, of open-...earth iron, 100 mm in diameter ...d 4 mm thick, was so mounted ...n a shaft that the center line of ...s face coincided with the center ...ne of the slot, *B*, against which ...he specimen was clamped. When ...he cam, *F*, working against a stop, ..., on the slide was turned to the ...roper position, the carriage, *C*, ...ounted on ball bearings, moved ...o the right until the specimen ...ested against the abrasion disk, ...he pressure between the two being ...etermined by the weights attach...d to the end of the slide.

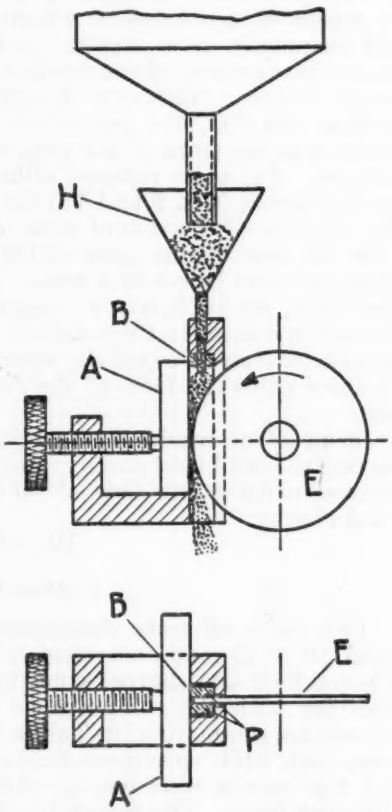

FIGURE 4.—*Diagrammatic sketch of essential parts of Brinell machine*

A hopper, *H*, above the slotted ...late was filled with sand fed into ... from the receptacle placed ...bove. During the test a contin...ous stream of sand was passed ...etween the specimen and the disk. ...he disk had a speed of 45 r. p. m., ...nd the linear travel of a point on ...ts circumference could be adjusted ...y a graduated wheel and lock nut, ..., on top of the machine. After ...he disk had run the predetermined ...istance, the motor stopped auto...matically. During the test the motor also actuated a small fan which ...sucked the used sand down into a bag. Figure 4 is a diagrammatic ...sketch illustrating the essential parts of the machine.

The principle of the test, then, is as follows: The plane surface of ...he test specimen is pressed under a definite load against the edge of ...a slowly rotating disk while a constant stream of standardized, fine-...grained sand is fed between the surface of the disk and the specimen. ...After the circumference of the disk has run through the distance

required for a test, the specimen is removed, washed, dried, and weighed, and the maximum depth of the segmentary groove produced is measured by means of a depth indicator reading directly to 0.01 mm. The wear-resistance number "Nm" is calculated from the formula $Nm=\frac{1,000}{A}$, where A is the volume in cubic millimeters of the worn-out segment for 1 mm thickness of disk. In tables furnished with the machine values of "Nm" are given for different values of diameter of disk and maximum depth of groove.

Two methods of expressing the resistance to wear as determined by the Brinell machine are (1) by means of the "Nm" numbers and (2) by means of the losses of weight. The former is rather unreliable and frequently gives erratic results, due to the difficulty of securing an accurate reading of the depth of the groove because of the relatively rough bottom. This error is aggravated by the human equation in reading the dial, the pointer of which wavers over an appreciable distance as the point of the gage is moved but slightly over the rough bottom. For these reasons, although the "Nm" numbers are given on the curves (figs. 9 and 13) the losses of weight have been used as the criterion of the rate of wear (or resistance to wear).

In the tests made, none of the abrading disks was used when its diameter wore below 97.5 mm. When a new wheel was used for the first time, its surface was roughened by first running it against a dummy specimen in the machine. During a test the edge of the disk often burred over, especially when the test specimen was of soft steel. In these cases the faces of the disk were dressed by a file after each test.

Inconsistent results were at first obtained by this machine. By sieving the sand used and by removing the two guide plates, P (fig. 4), thus allowing a free flow of sand, results were secured which gave good checks.

IV. RESULTS

1. BALL-MILL TEST

Two series of tests were made. In one, standard Ottawa silica sand, 20 to 30 mesh, was used, while in the other, Illinois glass sand, a much finer and sharper sand, was used. The results of these tests, together with the compositions and heat treatments of the steels tested, are summarized in Tables 1 and 2. All specimens marked "C" were cast, while specimens marked "F" were forged. Widely different test results were usually obtained on the same material during different tests. The reason for this is not at all clear.

Specimen	Composition	Condition	Unit loss, mg per square centimeter per hour×10³														Average last 10 24-hour runs
			15 hours			24 hours											
	Per cent																
0C1	0.41 C, 3.04 Ni, 0.72 Mn, 0.13 Si.	Normalized at 815° C	11.3	11.0	11.6	12.9	10.8	9.6	8.1	7.5	13.9	10.2	12.1	12.9	11.0	11.4	10.7
0C3			13.3	8.8	12.0	13.9	12.1	9.8	8.7	6.9	12.5	10.0	11.4	13.7	10.6	11.4	
0F1			2.0	8.9	10.9	15.2	12.4	10.1	7.4	8.0	14.8	10.7	10.7	12.4	12.1	11.8	10.5
0F2		Normalized at 815° C., oil-quenched from 815° C. and drawn at 100° C.	9.6	11.2	15.2	13.8	13.2	9.5	8.4	6.2	15.6	10.7	9.9	13.0	10.3	11.9	
0F3			13.2	11.8	15.5	14.8	9.8	10.1	5.8	6.8	10.5	9.9	10.9	12.5	10.3	10.7	9.6
0F4			12.8	11.5	10.5	16.2	9.8	9.7	6.0	6.8	11.1	9.7	10.7	11.1	9.7	9.7	
1C1	0.46 C, 0.97 Cr, 0.75 Mn, 0.14 Si.	Normalized at 815° C	9.3	9.3	11.6	13.1	10.2	8.5	6.9	6.7	12.5	8.5	9.8	12.7	9.8	10.6	9.6
1C3			18.9	10.6	12.3	13.1	11.2	8.1	8.3	5.4	11.5	8.3	11.8	11.2	9.1	10.4	
1F1			15.8	10.2	10.9	14.2	10.3	8.2	6.8	5.8	13.0	9.3	10.3	11.8	9.9	10.7	9.5
1F2		Normalized at 815° C., oil-quenched from 815° C. and drawn at 200° C.	19.9	10.3	11.0	14.7	9.8	9.4	7.5	6.2	11.1	8.9	10.0	12.1	9.4	9.3	
1F3			5.9	9.5	10.9	16.0	9.5	8.8	5.4	6.6	10.1	9.5	9.5	11.5	8.9	10.3	8.8
1F4			9.3	10.3	10.6	14.9	8.7	8.5	4.8	6.4	8.9	9.5	10.0	10.6	9.8	9.3	
3C1	0.43 C, 0.45 Mn, 0.09 Si.	Normalized at 815° C	22.0	12.3	24.7	15.4	14.9	11.0	10.6	9.6	15.2	14.6	12.7	16.0	12.5	12.1	12.6
3C3			18.9	12.9	14.6	16.2	15.2	10.6	7.9	9.5	14.9	11.4	11.2	16.0	11.6	13.1	
3F1			17.0	11.0	20.3	15.2	13.3	10.4	10.2	8.8	15.2	11.0	13.3	12.1	11.9	13.1	11.9
3F3		Normalized at 815° C., brine-quenched from 815° C. and drawn at 200° C.	12.6	10.6	12.6	14.5	9.3	8.9	5.0	6.8	10.0	9.3	10.2	11.0	9.4	10.0	9.0
4C1	0.46 C, 0.26 V, 0.71 Mn, 0.12 Si.	Normalized at 815° C	24.8	11.7	14.7	14.6	13.0	10.5	7.3	7.3	15.7	11.5	14.4	13.1	13.4	13.4	11.8
4C3			16.0	12.3	17.6	12.5	13.3	10.2	8.1	8.7	16.0	10.8	10.4	13.7	12.3	12.5	
4F1			+	8.6	12.6	13.1	11.2	8.9	7.5	7.1	12.7	9.8	10.4	14.5	11.0	10.4	10.6
4F2		Normalized at 815° C., brine-quenched from 815° C. and drawn at 200° C.	13.9	9.6	13.3	12.2	11.0	9.5	7.9	7.7	13.1	11.4	10.4	13.1	12.9	10.8	
4F3			9.3	11.6	8.6	14.7	10.4	8.3	5.8	6.4	9.8	8.9	10.4	10.6	9.6	10.2	8.8
4F4			11.3	11.0	10.3	14.3	8.7	8.3	5.8	6.4	9.6	8.5	10.4	8.9	8.9	9.6	
5C1	0.43 C, 0.46 Mo, 0.64 Mn, 0.13 Si.	Normalized at 815° C	14.0	11.0	11.0	13.6	10.8	9.6	7.9	6.5	15.0	10.4	11.2	11.9	10.6	12.1	10.8
5C3			14.3	10.0	12.3	14.5	13.1	10.0	7.7	6.6	13.9	10.4	11.0	12.4	10.8	13.1	
5F1			28.5	14.6	24.5	15.3	13.0	10.8	8.1	7.7	14.1	11.6	11.4	14.9	12.4	11.4	11.5
5F3		Normalized at 815° C., oil-quenched from 840° C. and drawn at 300° C.	14.6	11.0	13.3	14.5	9.8	9.6	6.0	7.1	10.6	9.6	10.2	11.4	9.6	9.1	9.3

Rockwell "C" hardness of all heat-treated samples was approximately 50.

TABLE 2.—*Results of the ball-mill test (Illinois glass sand)*

Specimen	Composition (per cent)	Condition	Unit loss, mg. per square centimeter per hour×10³												
			24 hours												Average last 10 runs
0C1	0.41 C, 3.04 Ni, 0.72 Mn, 0.13 Si.	Normalized at 815° C.	5.5	7.3	7.1	5.1	6.1	10.0	11.4	11.2	7.9	5.6	4.9	3.7	7.5
0C3			6.9	7.9	4.4	8.0	6.9	11.4	9.4	10.2	10.2	5.0	5.3	5.2	
0F1			5.8	7.2	3.5	7.9	6.6	14.0	13.0	12.0	6.0	5.8	4.8	4.9	
0F2		Normalized at 815° C., oil-quenched from 815° C. and drawn at 100° C.	5.4	7.2	5.1	8.5	5.0	10.0	13.0	11.1	7.2	6.0	4.8	6.8	7.8
0F3			3.7	6.0	4.7	6.1	3.4	11.8	6.8	7.2	4.5	4.9	4.8	4.9	
0F4			2.9	5.2	3.3	5.9	4.2	7.2	13.4	8.2	4.9	4.1	5.2	2.9	5.9
1C1	0.46 C, 0.97 Cr, 0.75 Mn, 0.14 Si.	Normalized at 815° C.	2.5	5.6	5.0	6.1	3.2	10.2	10.6	8.3	7.3	4.0	4.3	7.3	6.4
1C3			3.3	6.9	4.4	6.6	4.6	10.4	6.2	9.1	6.7	5.0	3.9	4.8	
1F1			4.9	4.3	3.9	6.3	5.0	8.4	9.7	9.1	6.0	4.9	6.2	4.7	
1F2		Normalized at 815° C., oil-quenched from 815° C. and drawn at 200° C.	2.5	6.2	2.9	6.4	4.4	8.7	7.5	8.7	2.7	4.2	4.3	2.5	5.8
1F3			2.1	4.5	5.8	4.5	4.0	7.4	10.1	6.6	4.9	3.5	4.8	4.9	
1F4			1.7	4.8	5.0	4.1	4.0	7.5	7.1	5.4	4.2	3.7	3.7	3.1	5.2
3C1	0.43 C, 0.45 Mn, 0.09 Si.	Normalized at 815° C.	6.0	8.5	6.7	10.3	7.9	12.3	14.2	10.4	9.6	7.3	8.4	5.0	8.8
3C3			6.0	7.7	5.6	10.0	6.7	11.8	10.6	11.6	9.3	7.5	4.9	6.2	
3F1		Normalized at 815° C., brine-quenched from 815° C. and drawn at 200° C.	7.1	9.4	5.4	7.8	7.5	11.0	10.8	11.9	7.3	6.0	6.7	7.5	8.2
3F3			2.3	6.0	3.7	4.9	4.2	8.3	6.6	6.2	6.2	3.3	4.1	3.7	5.1
4C1	0.46 C, 0.26 V, 0.71 Mn, 0.12 Si.	Normalized at 815° C.	6.1	8.6	5.6	7.2	6.7	9.6	11.1	11.3	5.6	5.9	4.9	3.7	7.4
4C3			4.0	6.9	5.2	6.1	5.5	11.6	9.4	10.2	9.1	6.6	6.5	5.4	
4F1			4.2	8.1	6.0	7.2	5.1	12.7	11.6	10.6	7.7	6.0	5.1	4.6	
4F2		Normalized at 815° C., brine-quenched from 815° C. and drawn at 200° C.	4.8	7.7	7.1	5.9	6.1	14.3	11.8	8.3	7.5	6.0	5.9	3.5	7.6
4F3			2.3	6.2	4.6	5.3	4.0	6.7	4.4	8.9	5.0	3.5	3.7	4.4	
4F4			1.9	6.0	3.7	4.1	4.4	8.9	6.4	7.5	5.4	4.0	4.5	2.1	5.1
5C1	0.43 C, 0.46 Mo, 0.64 Mn, 0.13 Si.	Normalized at 815° C.	3.8	8.7	2.7	8.0	6.3	9.6	11.2	10.2	5.6	8.3	6.1	6.4	7.3
5C3			5.0	6.7	5.0	7.2	6.3	9.5	8.1	11.0	8.9	4.2	4.5	6.0	
5F1		Normalized at 815° C., oil-quenched from 840° C. and drawn at 300° C.	6.8	8.7	4.8	6.9	5.4	13.9	9.1	9.1	9.1	6.2	3.4	4.8	7.3
5F3			2.9	5.2	6.7	6.6	4.0	10.8	6.4	8.5	5.6	5.4	5.1	4.2	6.3

Rockwell "C" hardness of all heat-treated samples was approximately 50.

In order to obtain some idea of the trends shown by the tests, the last ten 24-hour runs with each abrasive were averaged. The differences between the various steels are not very marked. It is of interest to note that the forged and hardened specimens in each group lost the least amount of weight. Generally speaking, the 0.97 per cent chromium steel was found to be the most wear-resistant steel in the series. Contrary to what might have been expected, in this type of test the finer, sharper sand (Illinois glass sand) caused less wear than the rounded Ottawa sand.

2. SAND-BLAST TEST

Figure 5 shows the results of tests on a series of steels, together with the compositions and heat treatments. Plotting the losses of weight against the amount of sand blasted on the specimens gave, after a wearing-in period, a straight-line relationship. The loss of weight of the specimen per unit amount of sand blasted was determined from the slope of the line. It was surprising to note that all the different steels, even when subjected to different heat treatments, showed about the same rate of wear. The very slight increase in rate of wear shown by heats No. 85046HM and 68290HM was not due to the steel, but to the use of a new sand-blast nozzle, as will be explained later.

The results of tests on a series of 0.45 per cent carbon steels, to show the effects of additions of Ni, Cr, and V as alloying elements, are shown in Figure 6. The sand used in these tests was different from the sand used for the tests summarized in Figure 5, therefore no obvious correlation between the two sets of curves is to be expected. Here, again, it was found that differences in composition and in heat treatment were not reflected by the resistance to wear, all steels showing the same rate of wear well within the limit of experimental error. The sand used in this test was standard Ottawa silica sand, 20 to 30 mesh in size, at an air pressure of 60 lbs./in.^{2}, and the loss of weight per 2 kg of sand blasted was about 0.095 g.

Sand-blast tests on some widely different materials are summarized in Figure 7, both at 30 and 60 lbs./in.^{2} pressure. The losses of weight when tested with the 30-pound pressure were considerably less than when tested under the 60-pound pressure, but the order of rates of wear was the same for the specimens.

In the tests under the 30-pound blast, no difference in resistance to wear was apparent between the two chromium-molybdenum steels, the 12 per cent manganese steel, and the white iron. Open-hearth iron showed a slightly higher loss of weight while gray iron lost considerably more.

The tests made under the 60-pound blast showed that there was no difference between the two chromium-molybdenum steels and the 12 per cent manganese steel. The white iron, however, showed a decidedly higher loss of weight, the open-hearth iron showed still more, and the gray iron again lost considerably more than any of the others.

It is apparent from the curves in the three figures just given that the sand-blast test is an extremely accurate test. As long as the same conditions of test existed, duplicate tests gave results which checked better than would be expected. The main variable difficult to control was the diameter of the sand-blast nozzle. This nozzle

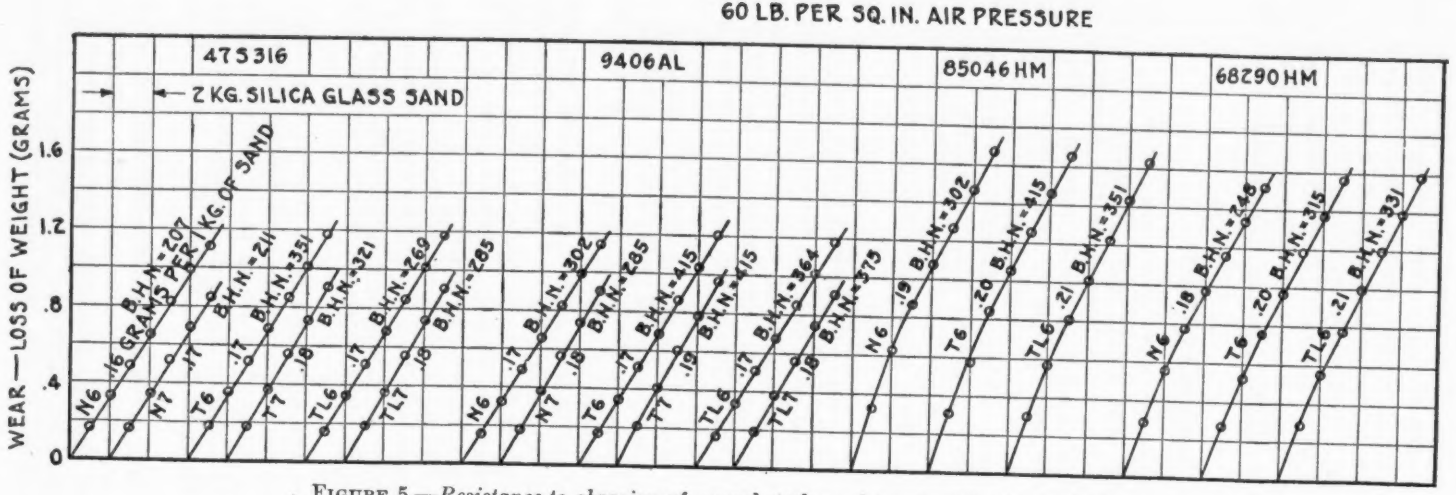

FIGURE 5.—*Resistance to abrasion of several steels as determined by the sand blast*

Heat No.	C	Mn	Heat treatment
	Per cent	*Per cent*	
47S316	0.64	0.53	N, normalized at 870° C.
9406AL	.70	1.13	T, normalized at 870° C., quenched in oil from 830° C., and tempered at 425° C.
85046HM	.63	1.79	
68290HM	.44	1.89	TL, normalized at 870° C. and quenched in lead at 400° C. from 830° C.

60 LB. PER SQ. IN. AIR PRESSURE

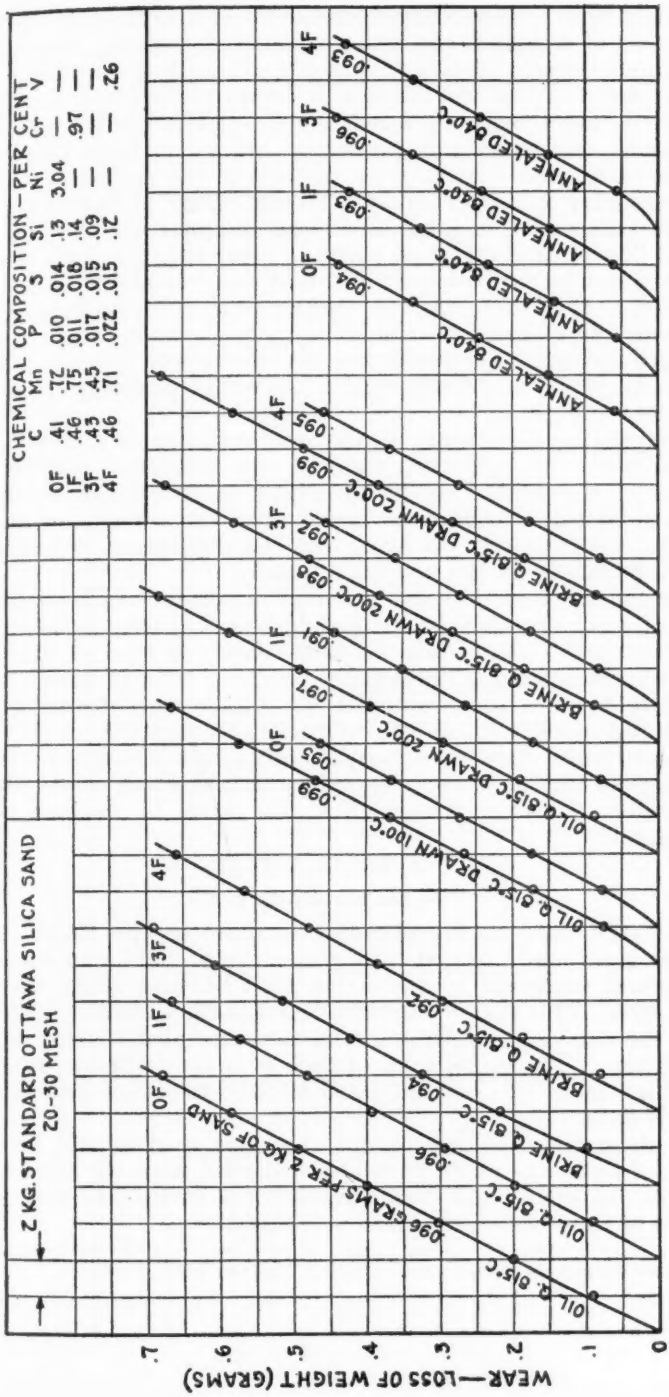

FIGURE 6.—*Resistance to abrasion of several steels as determined by the sand blast*

gradually wore and so enlarged, and as the area of the nozzle increas the losses of weight of the test specimens decreased. It was, the fore, imperative to replace this nozzle at frequent intervals.

The fact that this test failed to differentiate between various ste indicated that sensitivity was lacking. It is probable that the t conditions used were not proper to bring out large differences resistance to wear that may be inherent in the materials tested, a this reasoning is supported by a further study of the results.

If two materials, such as chilled iron and gray iron, be subjected a light flow of sand under no pressure other than the force of gravi it would not be surprising to find that one was about as resistant abrasion as the other. As the velocity of the blast of sand increas however, the chilled iron would begin to show its inherently hig abrasive-resistant qualities, and as the blast became still m severe, the difference between the two would probably become m and more apparent.

On applying this theory to the results shown in Figure 7, at le one difference is apparent, namely, the increased relative loss weight of the white iron to the steels at the higher pressure. appears logical, therefore, to reason that the severity of the tes still not great enough to bring out the differences in resistance wear inherent in all the materials tested.

The sharpness of the sand is also of importance in determining t rates of wear of materials. It should be noted from results shown Figures 5 and 7 that when the sand blast was used as the abradi medium, sharp sand (Illinois glass) produced rates of wear which w about four times those obtained on similar specimens tested wi larger and more rounded sand (Ottawa) at constant pressure.

These results show that many factors affect the rates of wear wi this type of test, so it would be expected that slight changes in actu conditions of service would affect the rates of wear of materi considerably.

3. BRINELL TEST

(a) SELECTION OF SAND

The sand used as the abrading medium in the Brinell test w Illinois glass sand [6] passed through a sieve of 0.297 mm. opening. was found necessary to sieve this sand because of its variation grain size. This size of sand was considerably smaller, incidentall than the size used by Brinell who recommended a grain size of 0. to 0.8 mm. The use of sand of such wide limits in size introduces variable which must be eliminated in order to secure definitely repr ducible data.

To determine whether or not the sand used should be dried, series of tests was made on cold-rolled steel with the sand as sieve and also as sieved and dried for 24 hours at 105° to 110° C. T results of these tests are shown in Table 3.

[6] Furnished through the courtesy of the Tavern Rock Sand Co., Toledo, Ohio.

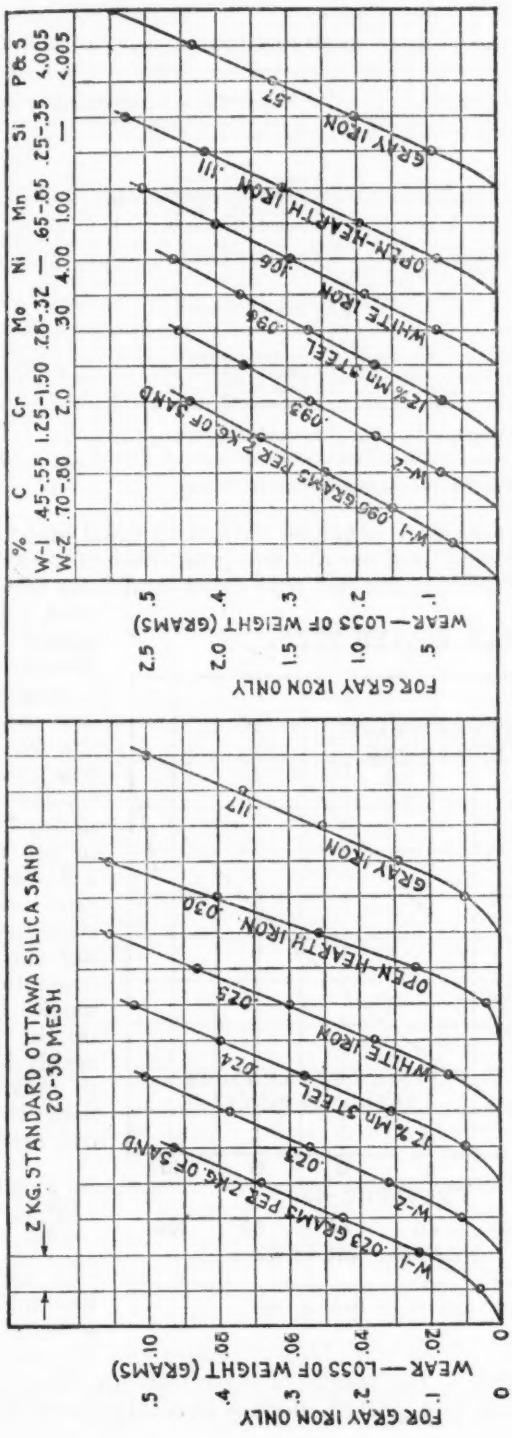
30 LB. PER SQ. IN. AIR PRESSURE
2 KG. STANDARD OTTAWA SILICA SAND 20-30 MESH
FOR GRAY IRON ONLY
WEAR — LOSS OF WEIGHT (GRAMS)
GRAY IRON
OPEN-HEARTH IRON
WHITE IRON
12% Mn STEEL
W-2
W-1
.023 GRAMS PER 2 KG. OF SAND
60 LB. PER SQ. IN. AIR PRESSURE
FOR GRAY IRON ONLY
WEAR — LOSS OF WEIGHT (GRAMS)
GRAY IRON
OPEN-HEARTH IRON
WHITE IRON
12% Mn STEEL
W-2
W-1
.090 GRAMS PER 2 KG. OF SAND
% C Cr Mo Ni Mn Si P & S
W-1 .45-.55 1.25-1.50 .20-.32 — .65-.85 .25-.35 <.005
W-2 .70-.80 2.0 .30 4.00 1.00 — <.005
W-1 AND W-2 QUENCHED IN AIR FROM 900°C AND DRAWN AT 510°C

FIGURE 7.—*Effect of sand-blast pressure on the resistance to abrasion of some materials*

TABLE 3.—*Comparison of dried and undried sand as abrasives in the Brinell test*

SAND NOT DRIED

Duration of test	Weight of sand passed through	Loss of weight	"Nu" No.
		g	
4 minutes 9⅘ seconds	4 pounds 5¾ ounces	0.1501	
4 minutes 10 seconds	4 pounds 5¾ ounces	.1443	
4 minutes 11 seconds	4 pounds 5¾ ounces	.1471	
4 minutes 18 seconds	4 pounds 7¾ ounces	.1528	
Average 4 minutes 12 seconds	4 pounds 6¼ ounces	.1486	

SAND AS DRIED

4 minutes 14 seconds	4 pounds 9 ounces	0.1380	
4 minutes 11 seconds	4 pounds 7½ ounces	.1362	
4 minutes 11 seconds	4 pounds 7½ ounces	.1332	
4 minutes 10 seconds	4 pounds 6¾ ounces	.1349	
Average 4 minutes 11 seconds	4 pounds 7¾ ounces	.1356	

Length of test run was 60 m and the pressure used was 10 kg.

Excellent checks were obtained with both dried and undried sand. The amount of sand used per test was greater when the dried sand was used, due, no doubt, to the fact that dried sand flows more freely than sand with some contained moisture. Despite the fact that a greater amount of dry sand was used, the loss of weight was greater with the smaller amount of undried sand used in the tests. Since a large volume of sand was sieved and stored, and since drying the sand under controlled methods would have slowed up the work considerably, it was decided to make all tests by using the sand without artificial drying.

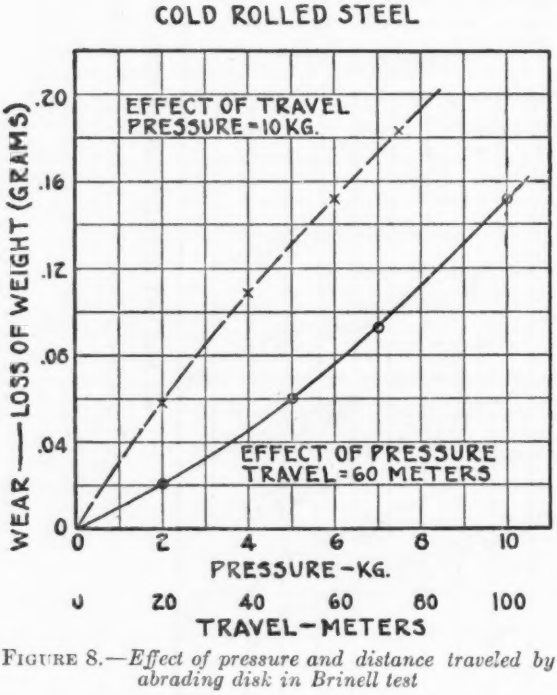

FIGURE 8.—*Effect of pressure and distance traveled by abrading disk in Brinell test*

(b) EFFECT OF PRESSURE AND OF DISTANCE TRAVELED BY DISK

A series of tests was made on cold-rolled steel to determine the effect of the variables—pressure and distance traveled by the abrading disk. The results of these tests are summarized in Figure 8. As would be expected, increase in total pressure caused a more

rapid loss of weight because of the greater proportional increase in pressure per unit of area, while increase in travel caused a smaller increase in loss of weight due to the decreasing average pressure per unit of area during the test (greater area of contact). For test purposes it was decided to make all runs at a pressure of 10 kg and 60 m travel of the disk.

(c) EFFECT OF CARBON CONTENT ON THE RESISTANCE TO WEAR

A series of steels varying in carbon content was tested as normalized, as normalized and annealed, and as normalized and hardened, to determine the effect of carbon content on resistance to wear. These results are summarized in Figure 9 together with the determinations of Rockwell and Brinell hardness. All points on the curves of wear are the average of four tests. The chemical compositions and heat treatments of these steels are given in Table 4.

TABLE 4.—*Compositions of the steels*

Mark	C	Mn	P	S	Si	Temperature—		
						Normalizing	Hardening	Annealing
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*°C.*	*°C.*	*°C.*
1D	0.078	0.482	0.099	0.083	0.018	970	940	920
1D	.203	.430	.006	.041	.027	940	910	890
2C	.425	.673	.044	.026	.223	865	835	815
3C	.573	.700	.013	.023	.200	830	800	780
4A	.762	.501	.028	.026	.276	810	775	755
5U	.81	.23	.024	.021	.28	810	780	755
6A	1.03	.345	.037	.036	.387	810	770	755
7U	1.29	.271	.011	.013	.250	925	770	755

All specimens were about one-fourth inch thick.
Time of holding at all temperatures, one-half hour.
All hardening by water quenching.
All specimens hardened or annealed were previously normalized.

The "Nm" wear-resistance numbers of these steels were very erratic for reasons previously mentioned and are considered of little value.

If the losses of weight of these steels are considered, it is evident that the percentage of carbon exerted a very marked influence upon the resistance to wear. An increase of carbon increased resistance to wear and this increase was greater in the lower range of carbon content than in the higher range. Furthermore, the resistance to wear of the hardened steels was greater than that of the normalized steels, which, in turn, showed greater resistance than the annealed steels. Comparing these trends with the curves of hardness shows in a convincing manner that the resistance to wear of carbon steels as determined by the Brinell machine is dependent upon the hardness.

The only point which is radically off the weight-loss curves is that for the annealed, 0.81 per cent carbon steel. It will be noted that the hardness of this steel was between the corresponding values for the 0.42 per cent and 0.57 per cent carbon steels and that the loss of weight also was between the corresponding losses of weight of these two steels. Thus, a decreased hardness was reflected by an increased loss of weight. Similarly, the normalized, 0.76 per cent

FIGURE 9.—*Effect of carbon content on the wear of carbon steels tested in Brinell machine*

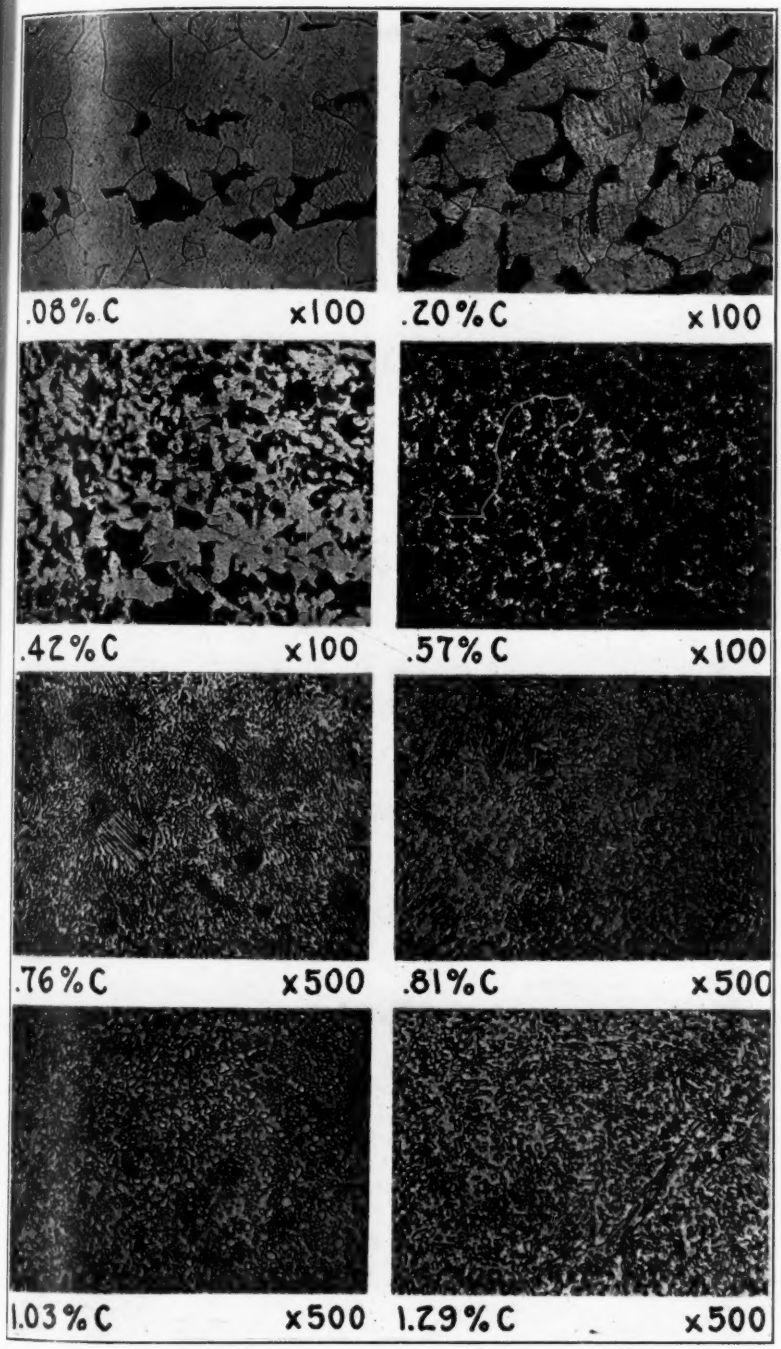

FIGURE 10.—*Microstructures of annealed carbon steels tested in Brinell machine*

Etched with 5 per cent picric acid in alcohol.

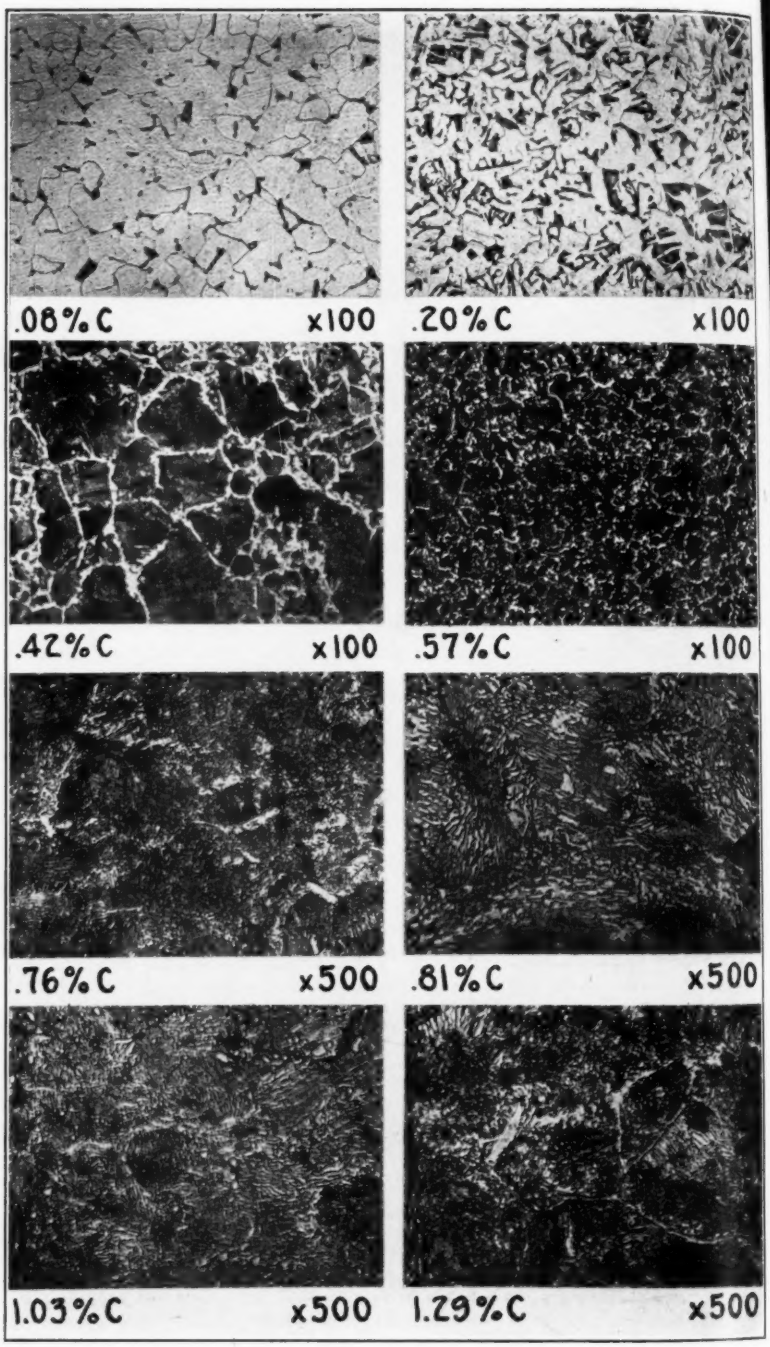

FIGURE 11.—*Microstructures of normalized carbon steels tested in Brinell machine*

Etched with 5 per cent picric acid in alcohol.

carbon steel showed a slightly higher hardness as judged by the curve of hardness and this was reflected by a decreased loss of weight. The microstructures of the annealed steels are shown in Figure 10, of the normalized steels in Figure 11, and of the hardened steels in Figure 12.

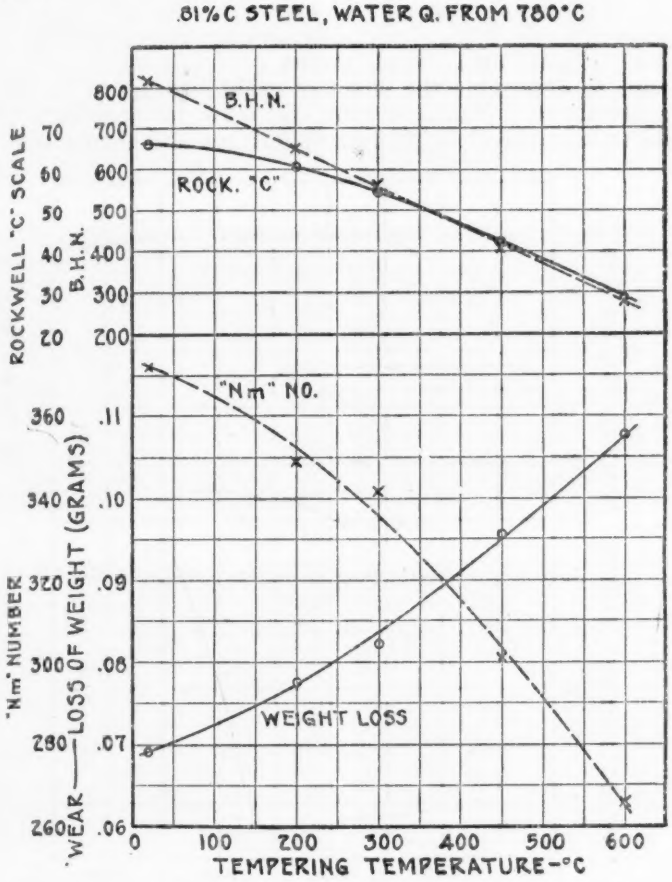

FIGURE 13.—*Effect of tempering temperature on the wear of an 0.81 per cent carbon steel tested in Brinell machine*

(d) EFFECT OF TEMPERING TEMPERATURE ON THE RESISTANCE TO WEAR

The effect of tempering temperature on the resistance to wear of the 0.81 per cent carbon steel was studied. All specimens were held for one hour at tempering temperature. The results of the tests (each point is the average of four tests), together with the hardness determinations, are summarized graphically in Figure 13. These curves show that increase in tempering temperature progressively lowers the resistance to wear of eutectoid carbon steel as determined by the Brinell machine.

The microstructures of these steels are shown in Figure 14.

(e) EFFECT OF ANNEALING TEMPERATURE ON THE RESISTANCE TO WEAR

There is a popular conception to the effect that the smaller the grain size of the steel, the greater the resistance to wear. This idea seems to be based, at least in part, upon the assumption that the larger the grain size, the more brittle the material and the more easily the individual grains may be torn out. As will be shown later in this report, in the type of abrasion investigated here the individual grains are not torn out as whole grains.

In order to determine the effect of grain size upon the resistance to wear, two steels (0.20 per cent and 0.76 per cent carbon) were annealed at successively higher temperatures and then tested. The

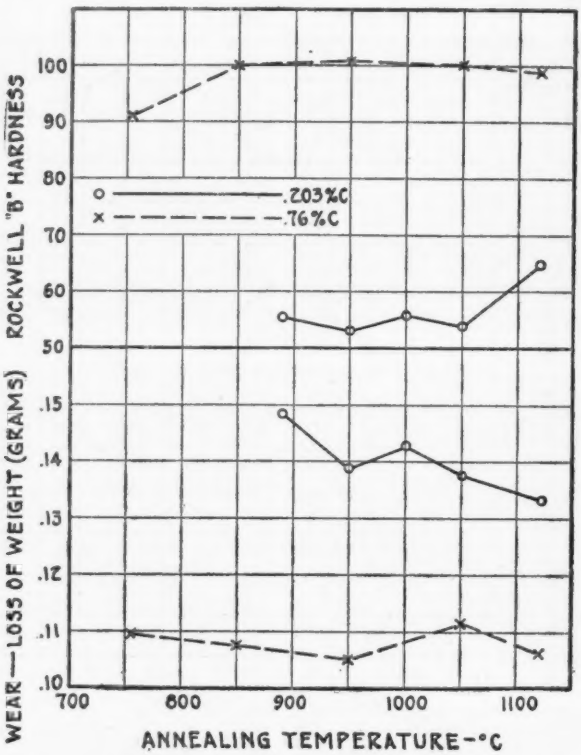

FIGURE 15.—*Effect of annealing temperature on the wear of a 0.20 per cent and 0.76 per cent carbon steel tested in Brinell machine*

samples were held one-half hour at each annealing temperature with the exception of the highest temperature, at which they were held for three and three-fourths hours. The results of these tests are summarized in Figure 15.

The effect of the temperature of annealing upon the resistance to wear of the 0.76 per cent carbon steel was very slight, but the effect on the 0.203 per cent carbon steel of increasing the temperature of annealing was rather marked, the resistance to wear increasing with the temperature. This is the reverse of what ordinarily would have been expected and no explanation of this apparent anomaly is offered.

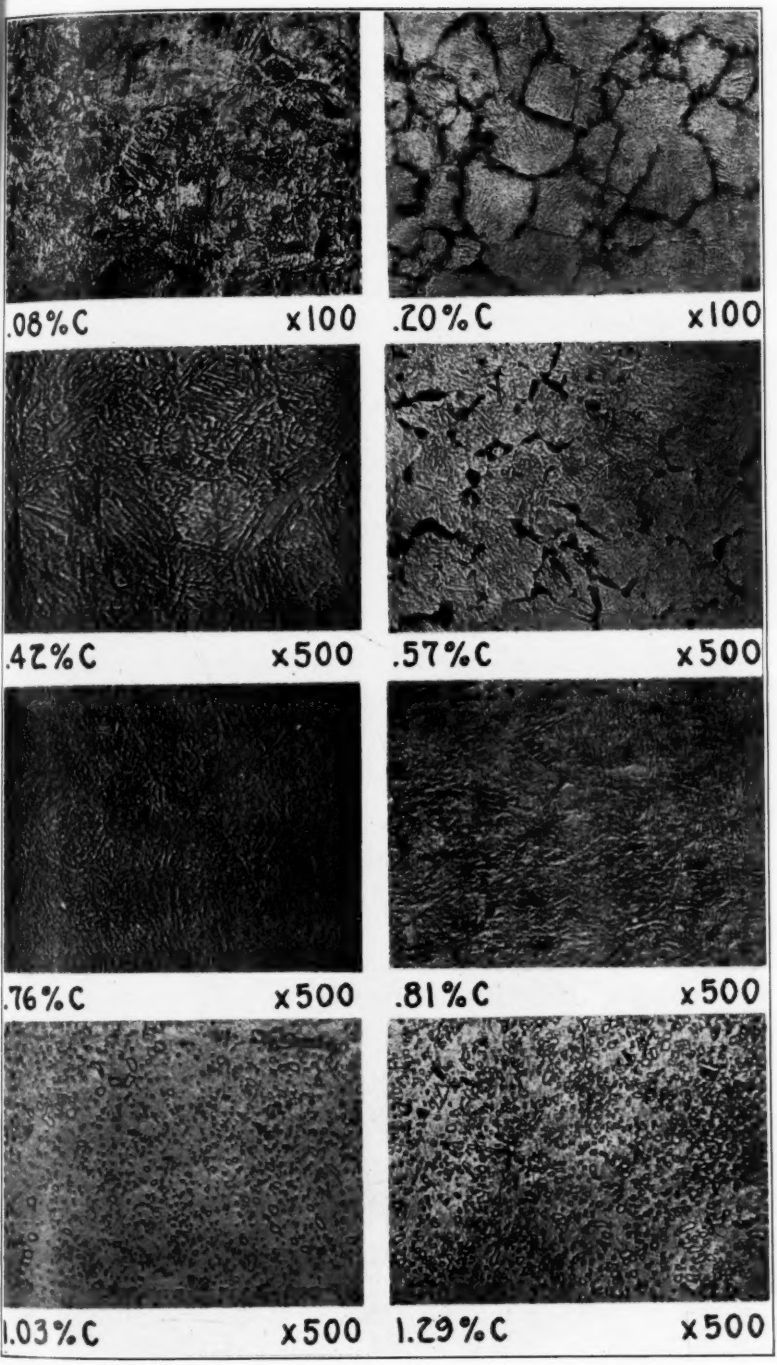

FIGURE 12.—*Microstructures of hardened carbon steels tested in Brinell machine*

Etched with 5 per cent picric acid in alcohol.

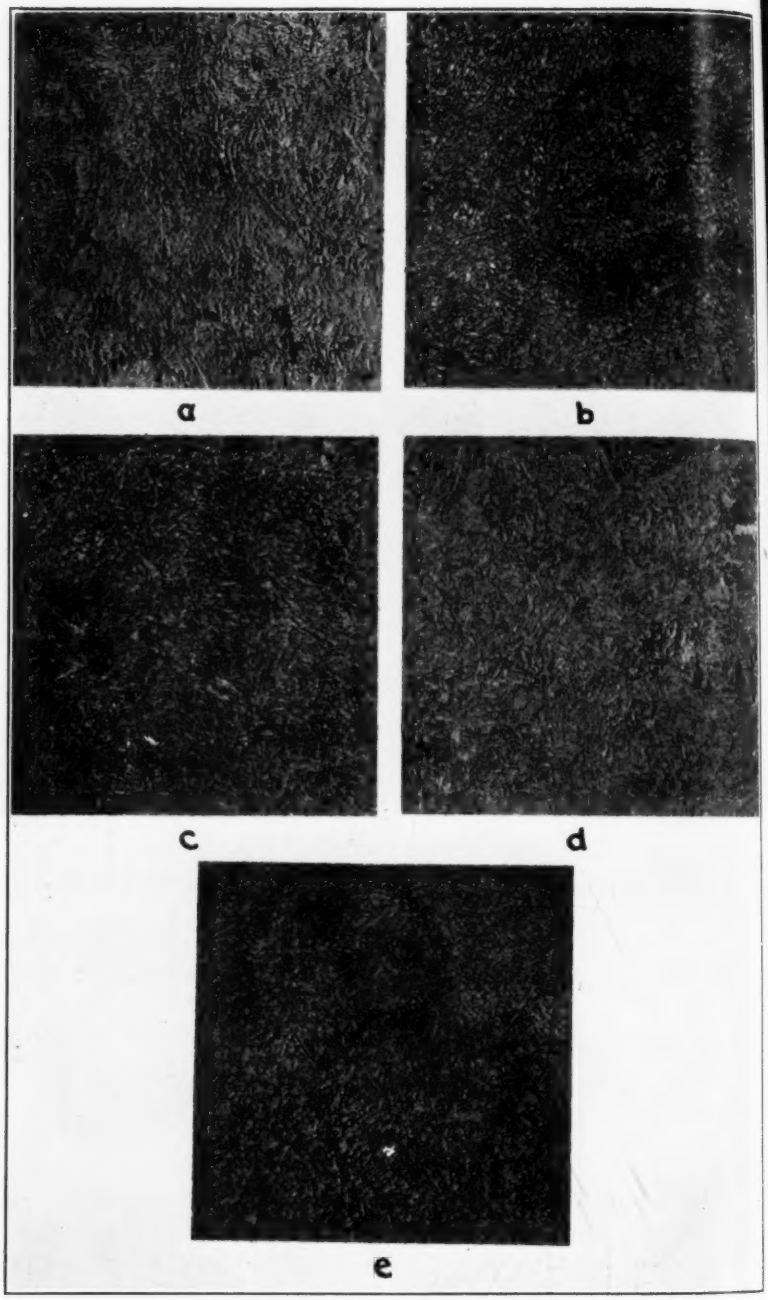

FIGURE 14.—*Microstructures of a tempered 0.81 per cent carbon steel tested in Brinell machine*

Etched with 5 per cent picric acid in alcohol. × 500. *a*, As hardened; *b*, tempered at 200° C.; *c*, tempered at 300° C.; *d*, tempered at 450° C.; *e*, tempered at 600° C.

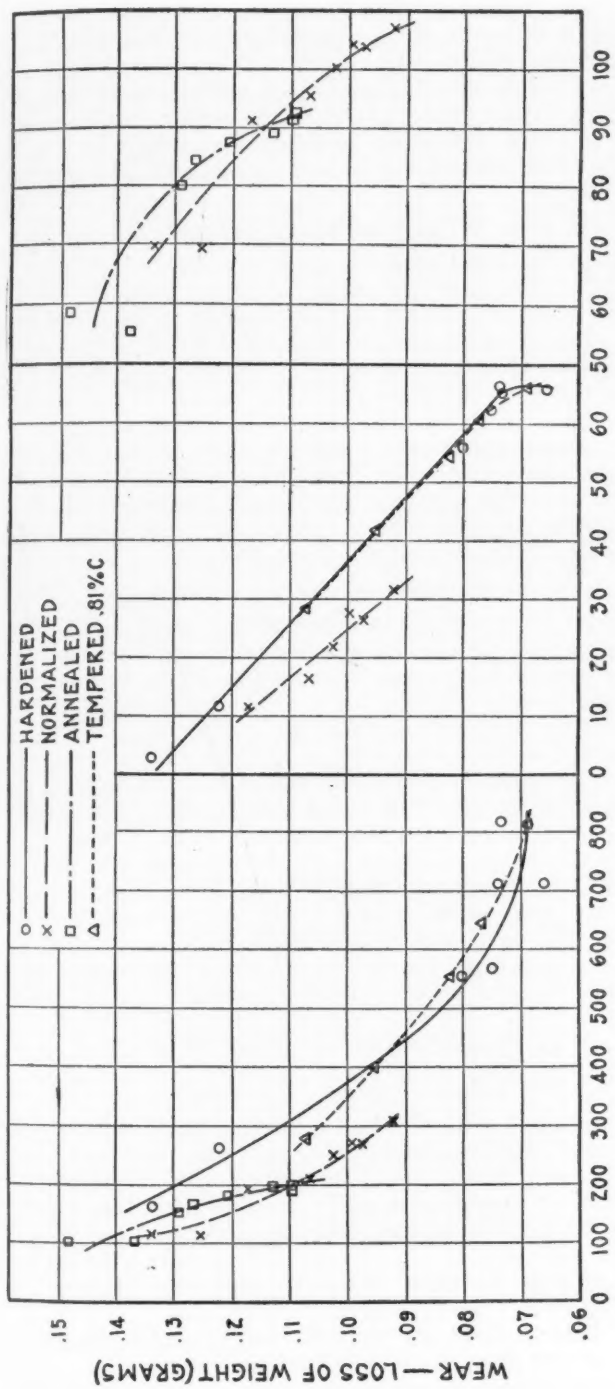

FIGURE 18.—*Effect of hardness on the wear of carbon steels as determined by the Brinell machine*

It may be noted, however, that increasing the temperature of an
nealing results in a trend toward higher hardness, and this is a fact
in causing increased resistance to wear. The microstructures of th
0.203 per cent carbon steel, annealed at various temperatures, ar
shown in Figure 16 and of the 0.76 per cent carbon steel in Figure 1
The increase in grain size is not so marked as might have been ex
pected, but the trend toward larger grains with increasing temperatur
is unmistakable.

(f) RELATION OF HARDNESS TO RESISTANCE TO WEAR

The fact that the wear as determined by the Brinell machine
influenced by the hardness has already been mentioned. In Figur
18 the data shown in Figures 9 and 13 have been replotted to sho
the effect of hardness on the loss of weight of the various carbon stee
These curves show that for increased hardness, the losses of weig
decrease; that is, the resistance to wear increases. This relationsh
is practically linear in the lower range of hardness numbers; in th
higher range, however, apparently large changes in hardness are no
accompanied by correspondingly great changes in resistance to wea
This may be due to the fact that the Brinell hardnesses of the har
steels were found to be unduly high, caused, perhaps, by the difficul
of reading accurately small Brinell impressions.

(g) EXAMINATION OF ABRADED SURFACES

In order to show the manner in which wear takes place on abrade
surfaces, the groove worn into an annealed 0.20 per cent carbon ste
was copper plated, and both cross sections and longitudinal sections
were cut for microscopic examination. The structures of these sam
ples at the wearing surfaces are shown in Figure 19.

The appearance of the surface both at right angles to the groov
and longitudinally through it is about the same. In both cases ver
marked evidence of localized flow in the form of strain lines is presen
This has also been found in wear-resistance tests of bronzes.[7] An
examination of the abraded surface (see, for example, fig. 19 (*b*)) als
reveals the fact that the mechanism of wear takes place by parts o
individual grains being abraded and not by grains being removed i
their entirety. This is what would be expected when it is considere
that at room temperatures the cohesive force between the grains i
greater than the internal strength of the grains.

V. DISCUSSION OF RESULTS

1. BALL-MILL TEST

The results obtained with the ball mill were quite erratic and wi
be dismissed as of qualitative value only. The ball mill does no
seem to hold much promise as a laboratory machine for testing th
resistance of metals to abrasion. The trouble with this machine i
twofold—it is not sufficiently sensitive to show positive differences
in resistance to wear and it is not sufficiently accurate to give che
results. In addition to these disadvantages the making of th
spherical specimens is a costly and tedious process.

These tests showed, however, that the forged and hardened spe
mens lost less weight than the normalized specimens.

[7] H. J. French, S. J. Rosenberg, W. LeC. Harbaugh, and H. C. Cross, Wear and Mechanical Proper
of Railroad Bearing Bronzes at Different Temperatures, B. S. Jour. Research, 1 (RP13); September, 19

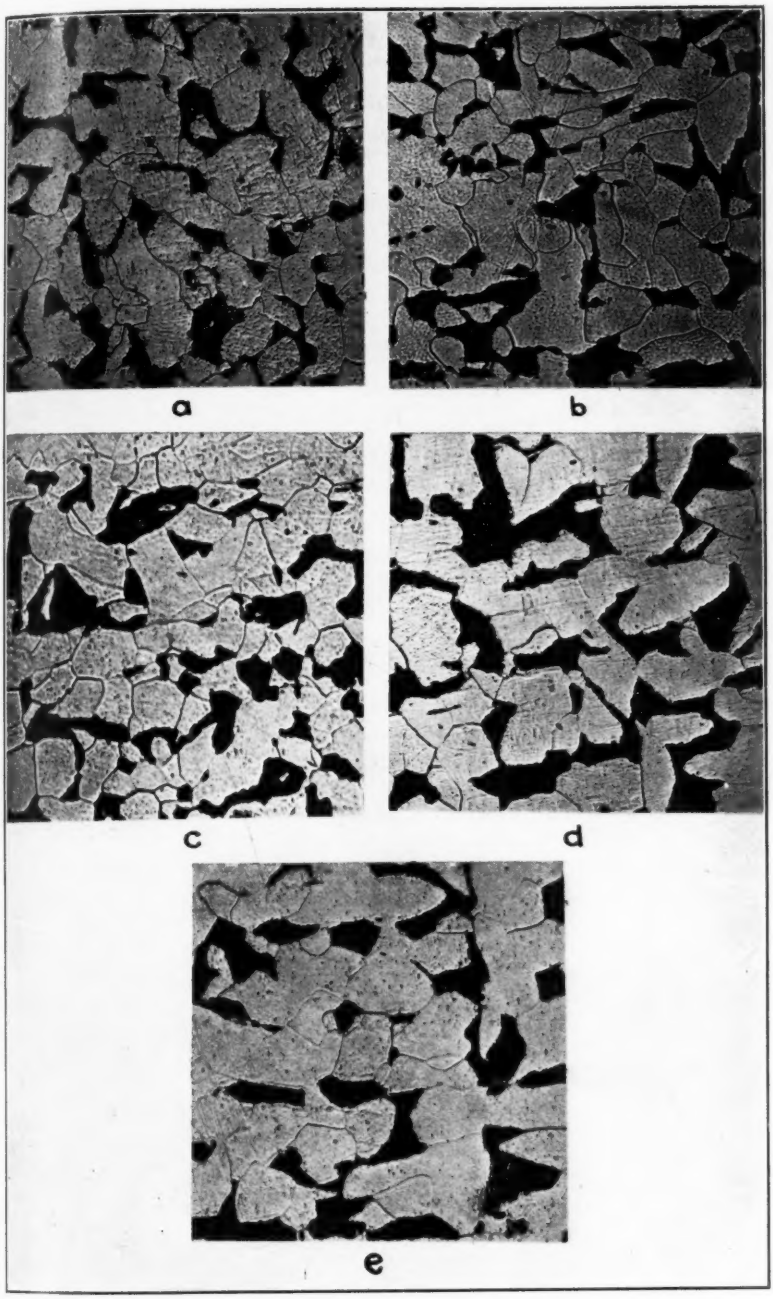

FIGURE 16.—*Microstructures of 0.20 per cent carbon steel annealed at different temperatures, tested in Brinell machine*

Etched with 5 per cent picric acid in alcohol. × 100. *a*, Annealed at 890° C. for one-half hour; *b*, annealed at 950° C. for one-half hour; *c*, annealed at 1,000° C. for one-half hour; *d*, annealed at 1,050° C. for one-half hour; *e*, annealed at 1,120° C. for three and three-fourths hours.

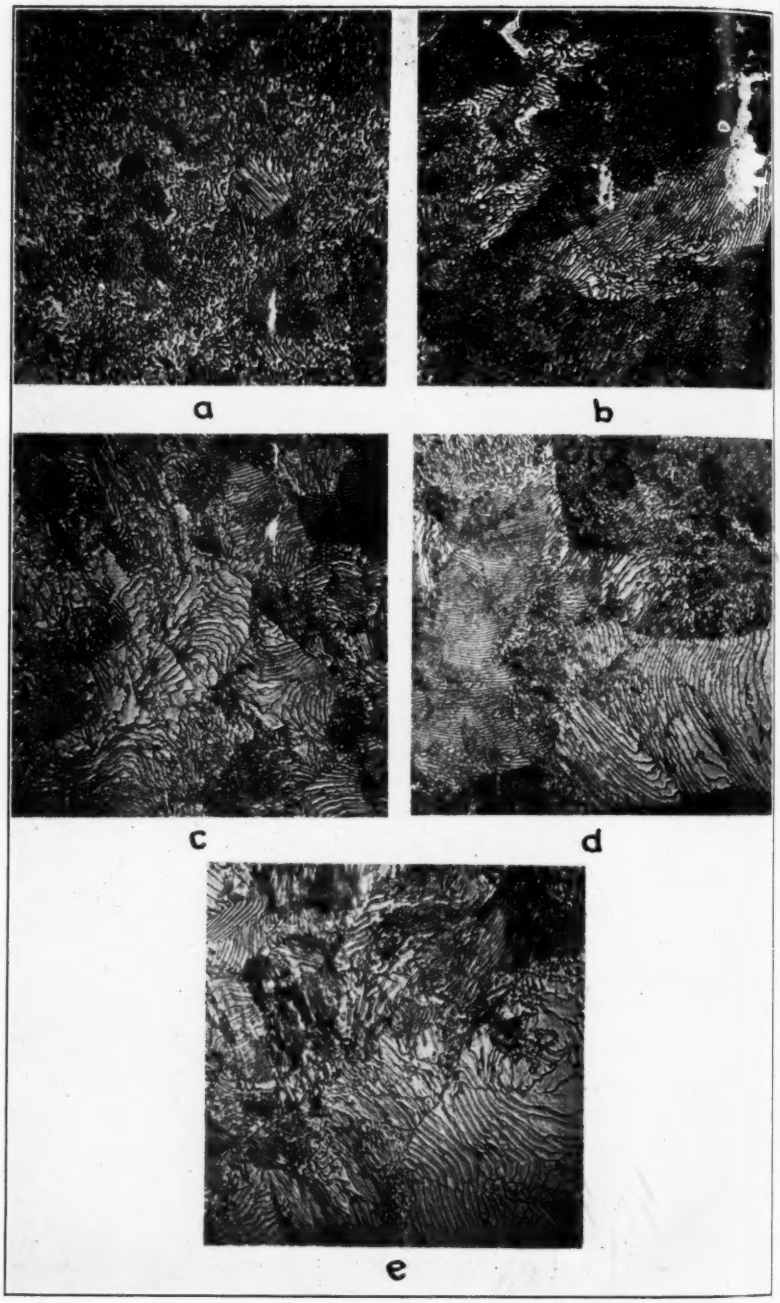

FIGURE 17.—*Microstructures of 0.76 per cent carbon steel annealed at different temperatures, tested in Brinell machine*

Etched with 5 per cent picric acid in alcohol. × 500. *a*, Annealed at 755° C. for one-half hour; *b*, annealed at 850° C. for one-half hour; *c*, annealed at 950° C. for one-half hour; *d*, annealed at 1,050° C. for one-half hour; *e*, annealed at 1,120° C. for three and three-fourths hours.

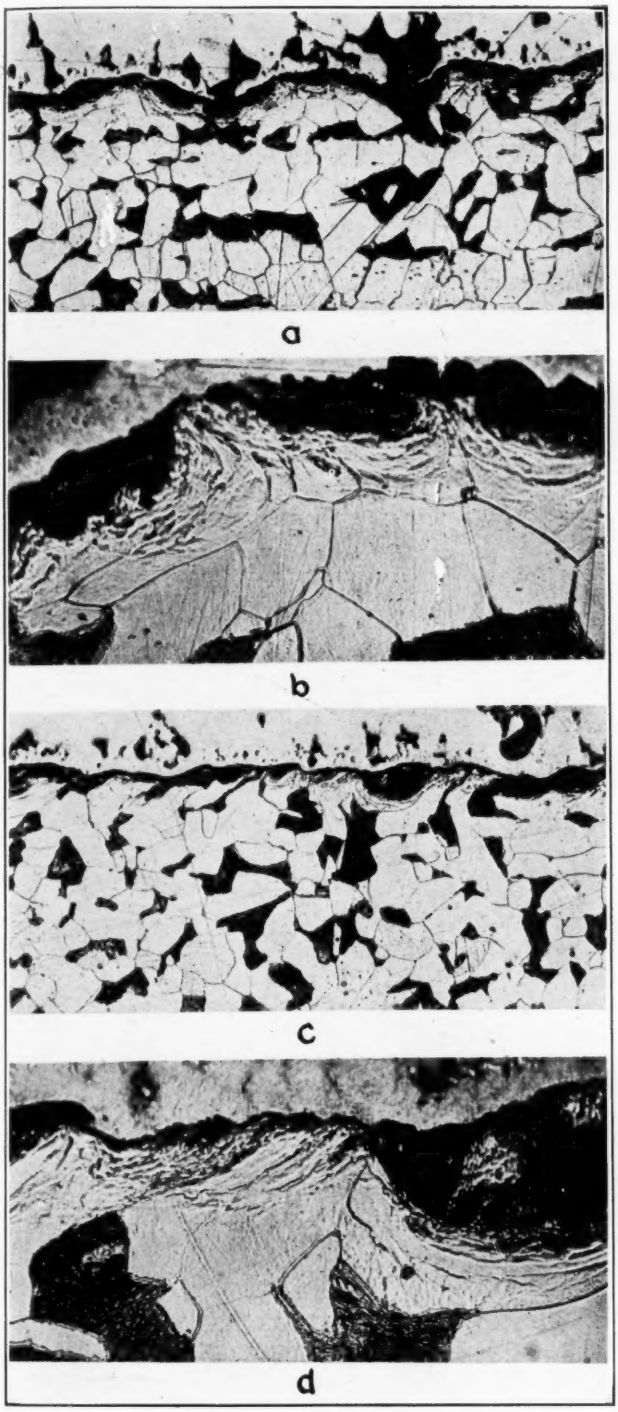

FIGURE 19.—*Micrographs of the structure adjacent to the abraded surface of an annealed 0.20 per cent carbon steel tested in Brinell machine*

Etched with 2 per cent nitric acid in alcohol. *a*, Cross section through bottom of groove. × 100; *b*, same. × 500; *c*, longitudinal section through bottom of groove. × 100; *d*, same. × 500.

2. SAND-BLAST TEST

The sand blast is a very rapid and accurate abrading medium. Of all the steels tested, however, no great differences were apparent between them. Practically the same rates of wear were obtained, for instance, on the same steel when normalized as were obtained when hardened. It is thought that this apparent lack of sensitivity was due to the fact that the abrading conditions were not sufficiently severe to bring out the inherent differences in wear characteristic of the materials tested. This opinion is based upon the fact that differences in resistance to wear between some materials were apparent at a blasting pressure of 60 lbs./in.^{2} that were not noticeable at a pressure of 30 lbs./in.^{2}.

3. BRINELL TEST

A series of carbon steels varying from 0.08 to 1.29 per cent carbon was tested in the normalized, annealed, and hardened conditions. The results of these tests showed that the resistance to wear of these steels in this special type of test was dependent upon the hardness. A study of the effect of tempering temperature upon the wear showed the same trend; that is, the resistance to wear increased with the hardness.

The effect of grain size upon the resistance to wear was studied by testing a 0.20 per cent and a 0.76 per cent carbon steel annealed at various temperatures. An increase in temperature of annealing resulted in a general increase in resistance to wear, as evidenced by a decreased loss of weight, this being more marked in the low-carbon steel than in the high-carbon steel.

A study of the mechanism of wear or abrasion showed that grains of the steel were not torn off in their entirety, but were worn away in small particles, the abrasion being accompanied by severe local grooving.

VI. SUMMARY AND CONCLUSIONS

Three devices for testing the resistance of metals to abrasion were studied—the ball mill, the sand blast, and the Brinell machine.

The ball mill proved to be very unsatisfactory, only qualitative results being obtained. Generally speaking, this type of test showed hardened steels to be somewhat more resistant to abrasion than the same steels in the normalized condition.

The sand blast proved to be a very rapid and accurate abrading medium, but failed to differentiate between many steels which were known to have widely different wear characteristics in different conditions of service. This apparent anomaly seems to be due to the fact that the abrasion was not sufficiently severe to bring out the differences in resistance to wear inherent in the steel and shows conclusively that slight modifications of test conditions will give different results on the resistance of different materials to wear.

The Brinell test showed that the resistance to wear of normalized, annealed, hardened, or tempered carbon steels increased with an increase in hardness. Increasing the temperature of annealing resulted in a slight increase in resistance to wear, the increase being more marked in a low-carbon than in a high-carbon steel.

Abrasion in this last type of test is caused by the wearing away of exposed sections of the individual grains and not by the removal

of the grains in their entirety. The abrasion is accompanied severe local straining due to cold working.

As slight variables in wear testing have been shown to give differ results, it should not be expected that wear-resistance tests made machines of this type will necessarily check special service condition where many variables are encountered.

VII. ACKNOWLEDGMENTS

The author is indebted to Dr. R. L. Dowdell, senior metallurgis for his kindly suggestions and criticisms, and to Houston Bab junior scientific aid, for his conscientious assistance in many of t tests.

WASHINGTON, April 18, 1930.

AN IMPROVED VICTOR-MEYER MOLECULAR-WEIGHT APPARATUS [1]

By Mildred M. Hicks-Bruun

ABSTRACT

The Victor-Meyer molecular-weight apparatus for determining vapor density modified to permit measurements at two pressures, one atmosphere and one-half atmosphere. By using Berthelot's method of limiting density most of the effects of departure from the perfect gas laws are eliminated. Experiments with hydrocarbons gave molecular weights differing from the theoretical by the following maximum deviations: Benzene, 16 experiments, 0.2 per cent; hexane, 4 experiments, 0.24 per cent; naphthalene, 4 experiments, 0.06 per cent.

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III. Calculation of the molecular weight	579
IV. Results with hydrocarbons	581

I. INTRODUCTION

The Victor-Meyer method for molecular-weight determinations in the vapor state, as ordinarily carried out, involves the assumption that the vapor obeys the Boyle and Avogadro laws at the temperature of the experiment. Since this temperature is seldom very much above the normal boiling point of the substance, the departure from the gas laws is by no means inconsiderable.

MacInnes and Kreiling [2] have shown that this source of error can be removed by calculating the molecular weight from the Berthelot equation and the critical-point constants of the substance and that when this is done the accuracy of the method is very materially improved.

For practical purposes, however, this procedure suffers from the disadvantage that in no actual case will the critical-point data be known, if the molecular weight is unknown. The obvious method of removing this difficulty is to make use of Berthelot's method of limiting density by carrying out the measurements at two pressures. This paper describes an apparatus and technic by means of which this can be conveniently accomplished.

[1] This study was undertaken in connection with an investigation on "The Separation, Identification and Determination of the Chemical Constituents of Commercial Petroleum Fractions" listed as project No. 6 of the American Petroleum Institute research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] MacInnes and Kreiling, J. Am. Chem. Soc., **39**, p. 2350; 1917.

II. APPARATUS AND PROCEDURE

A method for using reduced pressure in determining the vapor density of substances which have high boiling points and which may decompose at high temperatures, has been developed by Lunge and Neuberg.[3] Their procedure was to measure the volume of air displaced by a definite mass vaporized at a known temperature and pressure. No application of this work to the determination of molecular weights was made at this time. However, later applications have been made, notably by Ramsay and Steele,[4] whose work will be discussed later in this paper.

In the present work, the objective is to determine molecular weights both accurately and rapidly, and without the use of the critical data. For this purpose two complete measurements are necessary. One is made at one atmosphere and the other at one-half atmosphere. The apparatus used is a modification of the Victor-Meyer type. It was designed to gain compactness of form, thus avoiding the well-known difficulties of local temperature differences which result from undue length of the vaporizing chamber.

However, a short vaporizing chamber greatly increases the possibility of errors resulting from diffusion of the vapor, which may condense in the adjoining burette. Diffusion is particularly liable to occur when the experiment is being carried out under reduced pressure. This possibility has been practically eliminated in the vaporizing unit shown in Figure 1.

The vaporizing chamber is about 40 cm in length, about 7 cm outside diameter, and has a capacity of approximately 1 liter. It is made of heavy-walled pyrex glass. It consists of an inner tube, *E*, of 10 mm outside diameter, surrounded by a series of bulbs of consecutively diminishing volume, *J* to *G*. The connections between the bulbs are tubes 11 mm in diameter, which provide a narrow gas passage between the bulbs. A quick, jerky displacement of the air which may result from the sudden release of the vapor in a single unrestricted vaporizing space, is thus avoided. The volume of the vapor formed by the sample is considerably less than the volume of bulb *J*. If a portion of the vapor should diffuse out of this bulb, it would obviously be greatly diluted in the succeeding bulb, and the effluent air from *G* should be free from the vapor.

The tube inclosed by the vaporizing chamber ends about 3 cm above the bottom of bulb *J*. It projects through a ring seal at the top of *G*, and is flared with a shoulder *C*. It has an enlarged opening, which is fitted with a ground glass stopper *B* for convenience in introducing the bulb containing the sample.

Two tungsten wire leads (diameter about 1 mm) are sealed through the stopper *B*. These are accessory to the breaking apparatus. Two designs of breaking apparatus have been employed. They are shown in details 1 and 2 of Figure 2. Both are made of brass and will fit closely (allowing for expansion) into the inner tube *E*. Unit 1 is fitted into a cork ring, which rests on the shoulder, *C*, and is used with the stopper *B*. It extends about 2.5 cm below tube, *E*, and is perforated with 3 mm openings. The sample bulb is introduced through

[3] Lunge and Neuberg, Ber., **24**, p. 729; 1891.
[4] Ramsay and Steele, Z. phys. Chem., **44**, p. 348; 1903.

a threaded plug at the bottom. The plunger, *H*, rests on the bulb. A steel weight, *D*, is suspended by a silk thread from a 0.5 ampere fuse wire across the tungsten leads *A*. A small electrical current is passed through these leads in order to melt the fuse wire and release the weight, *D*. The impact of *D* on the plunger, *H*, shatters the capillary tip of the bulb and allows the vapor to escape.

The alternate design 2 is used without the ground-glass stopper *B*. It is inserted through a cork stopper, which is fitted under flange *V*. It is then placed in the opening, *C*, and sealed with deKhotinsky cement. The plunger, *H*, is controlled by a rod at the upper end, threaded which passes through the fixed nut *P* and the double flange *V*. The flange is made vapor tight by a special packing of asbestos fiber and graphite. The plunger is operated by turning *T*.

The sample bulb is made from pyrex glass tubing 4 mm in diameter and of calculated length. Each end is drawn down to a small capillary tube. A fine scratch is made about 8 mm from the end of each capillary. The bulb is weighed and then filled with the substance. To accomplish this, one of the capillary ends is immersed in the substance (in liquid form) and slight suction applied to the other end. The bulb must have sufficient strength and contain enough vapor space to withstand the pressure from expansion of the sample when it is brought to equilibrium temperature within the vaporizing chamber. Before sealing the ends of the bulb, the air remaining in the space left for expansion is displaced by vapor from the gently heated substance. The capillary ends are then sealed in the tip of an oxy-gas flame. The bulb is weighed again and the weight of the sample is obtained by difference. The bulb is then placed in the breaking apparatus, which, in turn, is adjusted to position in the vaporizing chamber.

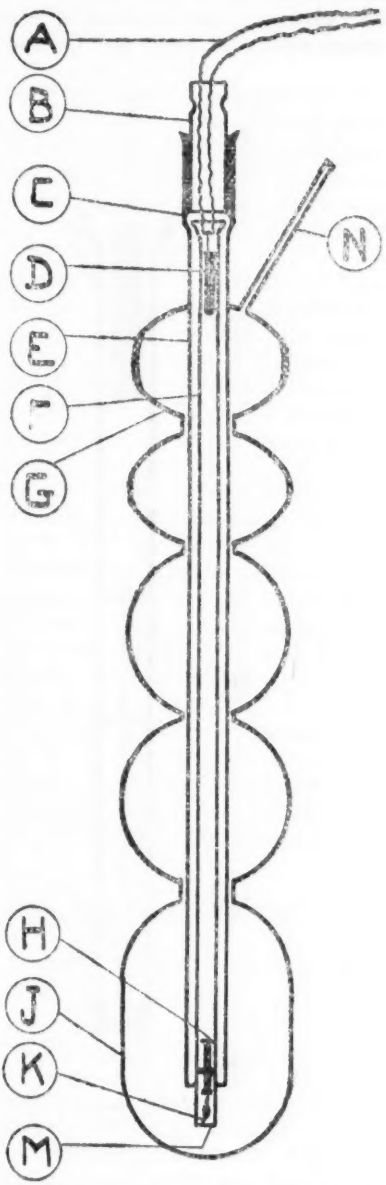

FIGURE 1.—*The vaporizing unit with breaking apparatus*

(1) Shown in position.

The vaporizing chamber is surrounded by an oil bath, which is kept within 0.05° C. of the proper operating temperature by an inclosed mercury-in-glass thermostat. Uniformity of temperature is insured by vigorous mechanical stirring. The bath is maintained at a temperature at least 50° C. above the boiling point of the substance

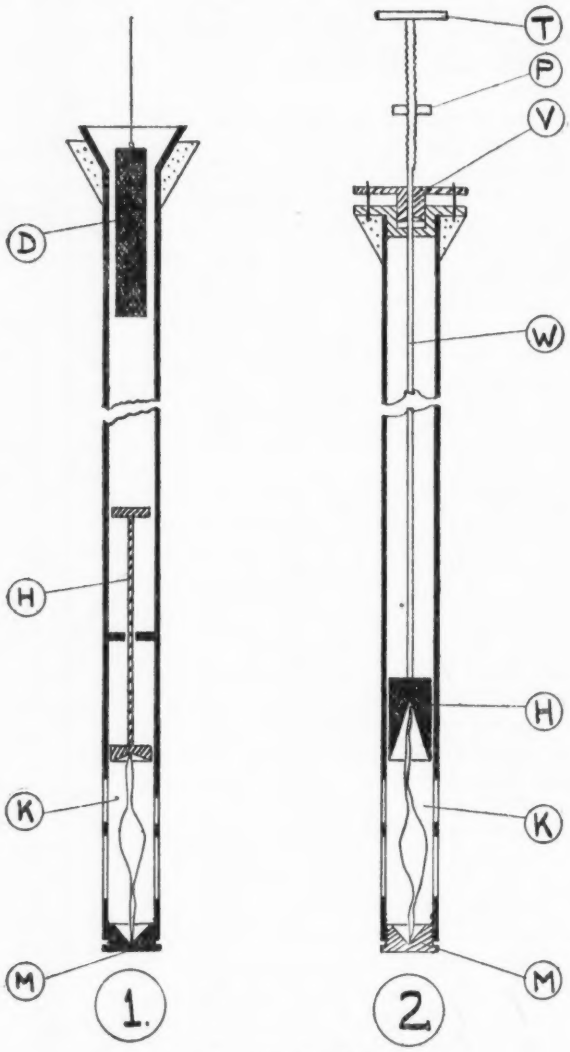

FIGURE 2.—*The breaking units*

to be vaporized. The constancy of the temperature control may be checked by treating the apparatus as a constant pressure gas thermometer.

The volume of the vaporized sample is obtained by measuring, at room temperature and a known pressure, the volume of air which it displaces. The technic and assembly of the manometric apparatus

mployed are identical with those used by this bureau[5] in gas analysis, ith the exception that the manometer is made longer and provided ith an additional platinum contact to facilitate measurements at 0.5 atmosphere. Provision is also made for partial evacuation of the pparatus and for filling it with nitrogen instead of air in cases where racking or oxidation of the substance is to be feared.

The capillary outlet from the vaporizing unit is adapted to the onnecting tube of the measuring system by means of a ground-glass oint sealed with a lubricant which will withstand high temperatures. A flexible glass coil, of thin walled, soft glass tubing about 2 mm in iameter, is placed between the joint and the manometer stopcock. his expansion coil permits connecting the rigidly fixed burette to he vaporizing unit.

The technic employed in a complete operation is as follows: The mple bulb, which has been placed in the apparatus as previously escribed, is allowed to remain in position until temperature equiibrium (about two minutes) is established throughout the chamber. uring the interval of time allowed for this to take place, adjustments re made in the measuring system to establish equality of pressure roughout. When equilibrium has been attained and the pressure alance established, the barometric reading is recorded (for atmosheric pressure) and the compensator is closed. The bulb conining the sample is then crushed. The stopcocks and leveling ulb of the burette are adjusted to allow the mercury level to fall owly, and the air displaced by the vaporized substance to flow over to the burette. Care is taken to prevent a sudden rush of air and sulting inequalities of pressure which may cause diffusion of the apor and consequent errors resulting from condensation. When here is no further displacement apparent, time is allowed for the mperature equilibrium in the burette to be reestablished. The ressure is again adjusted to the known pressure of the compensator. he volume and temperature of the air in the burette are recorded.

For the measurement made at the lower pressure, the above proedure is repeated except that the pressure balances are established t 0.5 atmospheres by partially evacuating the apparatus at the eginning of the determination.

III. CALCULATION OF THE MOLECULAR WEIGHT

The Berthelot equation for limiting density, rearranged to give the olecular weight, is as follows:

$$M=\frac{mRT}{pv}(1+Ap) \qquad (1)$$

here M is the molecular weight, R is the gas constant, and A is a oefficient which represents the deviation from the perfect gas laws. he experimental values for m (mass), T (temperature in degrees bsolute), p (pressure in atmospheres), and v (volume) are first subituted from the data obtained in the series of observations at ap-

[5] Shepherd, B. S. Jour. Research, **4**, p. 3; 1930.

proximately one atmosphere and in the series at approximately
atmosphere pressure and the resulting equations added together th

$$M_1+M_2+M_3+\ldots\ldots M_n=\frac{D_1RT_1}{P_1}(1+Ap_1)+\frac{D_2RT_2}{p_2}(1+Ap_2)$$

$$+\frac{D_3RT_3}{p_3}(1+Ap_3)+\ldots\ldots\frac{D_nRT_n}{p_n}(1+Ap_n)=R\frac{D_1T_1}{p_1}$$

$$+\frac{D_2T_2}{p_2}+\frac{D_3T_3}{p_3}+\ldots\ldots\frac{D_nT_n}{p_n}+A\ (D_1T_1+D_2T_2+D_3T_3$$

$$+\ldots\ldots D_nT_n)$$

which has the form:

$$M=R(C_1+C_2A)$$

Likewise the equations for 0.5 atmosphere may be reduced to:

$$M=R(C'_1+C'_2A)$$

or

$$C_2A-C'_2A=C'_1-C_1$$

and

$$A=\frac{C'_1-C_1}{C_2-C'_2}$$

The value of A so calculated is now substituted in equation (1) an the molecular weight is calculated for each determination.

In the above calculation it is assumed that the vapor density is linear function of the pressure, or rather, that the straight line throug the plotted determinations at one and at one-half atmosphere pass through the correct value of the limiting density for zero pressur This is not strictly true. The magnitude of the discrepancy is, how ever, small as can be shown by an examination of the data obtained b Ramsay and Steele.[6]

These investigators determined the vapor density for a number substances at a series of pressures ranging between 40 and 755 m of mercury. The molecular weights obtained from their data b means of a linear extrapolation through the points at one and at on half atmosphere are close to the true molecular weights, although no in general, as close as are the values obtained by extrapolating th actual curves through their observed points. The discrepancies ar however, small in both cases, and are within the experimental erro of the technic of the present method. These comparisons are show in Table 1.

[6] See footnote 4, p. 576.

TABLE 1.—*Comparison of molecular weights obtained by different methods from Ramsay and Steele's measurements* [1]

	Molecular weight		Per cent difference (b)–(a)	Molecular weight by linear extrapolation (c)	Per cent difference (c)–(a)	Molecular weight from gas laws (d)	Per cent difference (d)–(a)
	True (a)	Bygraph. extrapolation (b)					
Diethyl ether	74.077	73.95	−0.17	73.75	−0.42	74.84 at p=605 mm.	+1.04
Methyl alcohol	32.031	32.03	−.003	31.97	−.11	32.264 at p = 517 mm.	+.73
Benzene	78.046	78.15	+.13	77.94	−.15	79.71 at p = 755 mm.	+2.13
Octane	114.14	114.57	+.38	114.48	+.30	118.84 at p = 573 mm.	+3.33
Hexane	86.108	86.03	−.09	85.85	−.30	88.05 at p = 607 mm.	+3.41
Diisobutyl	114.14	114.19	+.03	113.84	−.26	118.59 at p = 565 mm.	+3.90
Toluene	92.062	92.46	+.43	91.89	−.19	93.95 at p = 671 mm.	+3.15

[1] Ramsay and Steele, Z. phys. Chem., 44, p. 348; 1903.

The largest differences resulting from the use of either method of extrapolation are approximately 3 parts in 1,000, while those resulting from the direct application of the ideal gas laws are of the order of 1 to 4 parts in 100.

IV. RESULTS WITH HYDROCARBONS

In this investigation the molecular weight has been determined for benzene,[7] synthetic *n*-hexane,[8] *n*-hexane from petroleum [9] and naphthalene.[10]

Three sets of results are given for the *n*-hexane from petroleum as it was known to contain carbon dioxide, water, and other impurities. For the first measurement no purification of the sample was made. For the second measurement the carbon dioxide was removed by heating the substance to the boiling point, under reflux, and bubbling air through the liquid. For the third measurement the hexane was distilled from metallic sodium to remove the water.

The correction for the liquid volume of the sample was made. The additional small correction for the vapor space left in the bulb was found to be of approximately the same size as and of opposite sign to the one for the dissolved air in the sample (0.08 per cent for benzene). These were considered to cancel each other. The weights were corrected ad vacuum.

Table 2 shows the values for the calculated molecular weight of benzene and their differences from the true molecular weight. The value found for the coefficient A for benzene is 0.0244. The value, calculated from the critical-point constants, is 0.0224.

Tables 3 and 4 give the experimental molecular weights for naphthalene, synthetic *n*-hexane, and the *n*-hexane from petroleum. The value found for the coefficient A for naphthalene is 0.00823. Since naphthalene is subject to decomposition, its critical temperature and pressure are unknown.

[7] Benzene (C. P. grade) was treated with concentrated H_2SO_4 and subsequently washed with dil. NaOH and water. It was recrystallized and then distilled from metallic sodium. It had a freezing range less than 0.2° C.

[8] Obtained from Eastman Kodak Co. Refractive index, $n_D^{20} = 1.376$.

[9] Bruun and Hicks-Bruun, B. S. Jour. Research, 5, October, 1930.

[10] Naphthalene (C. P. grade) sublimed and recrystallized. Freezing range less than 0.2° C.

TABLE 2.—*Experimental data for molecular weight of C_6H_6*

Molecular weight calculated from measurements at 1 atmosphere	Per cent difference from true value 78.046	Molecular weight calculated from measurements at 0.5 atmosphere	Per cent difference from true value 78.046
78.06	+0.02	77.93	−0.15
78.13	+ .10	78.07	+ .03
78.01	+ .05	77.95	− .12
77.90	− .19	77.99	− .08
77.90	− .19	77.96	− .11
78.00	− .06	78.13	+ .10
78.08	+ .05	77.97	− .09
77.99	− .08	78.07	+ .03
Mean = 78.01	Average deviation, 0.10 per cent. Maximum deviation, 0.19 per cent.	Mean = 78.01	Average deviation, 0.09 per cent. Maximum deviation, 0.15 per cent.

TABLE 3.—*Experimental data for molecular weight of $C_{10}H_8$ and synthetic C_6H_{14}*

Experimental molecular weight for $C_{10}H_8$	Per cent difference from true value 128.06	Experimental molecular weight for C_6H_{14} synthetic	Per cent difference from true value 86.108
128.02	0.04	86.26	+0.17
128.00	.06	86.32	.24
128.00	.06	86.18	.08
128.00	.06	86.15	.05
Mean=128.00	Average and maximum deviation, 0.06 per cent	Mean=86.23	Average deviation, 0.14 per cent; maximum deviation, 0.24 per cent

TABLE 4.—*Experimental data for "n-hexane from petroleum"*

[Purity, about 92 mole per cent]

[Showing the effects of dissolved moisture and carbon dioxide]

Experimental molecular weight before removing CO_2 and H_2O	Experimental molecular weight after removing CO_2	Experimental molecular weight after removing CO_2 and H_2O
84.61	85.42	85.58
84.49	85.47	85.61
Mean=84.55	Mean=85.45	Mean=85.60
	Increase=1.07 per cent	Increase=0.19 per cent

The mean precision which this apparatus has been found to give is approximately 3 parts in 1,000. The accuracy of the molecular weight obtained is about 2 parts in 1,000. The maximum deviations and the difference between the mean experimental value and the true molecular weight of benzene are shown in Figure 3 by lines drawn

through a plot which has been made of the 16 experimental values obtained. The greater discrepancy (6 parts in 1,000) in the case of the final results for the *n*-hexane from petroleum is attributable to impurities which were known to be present.

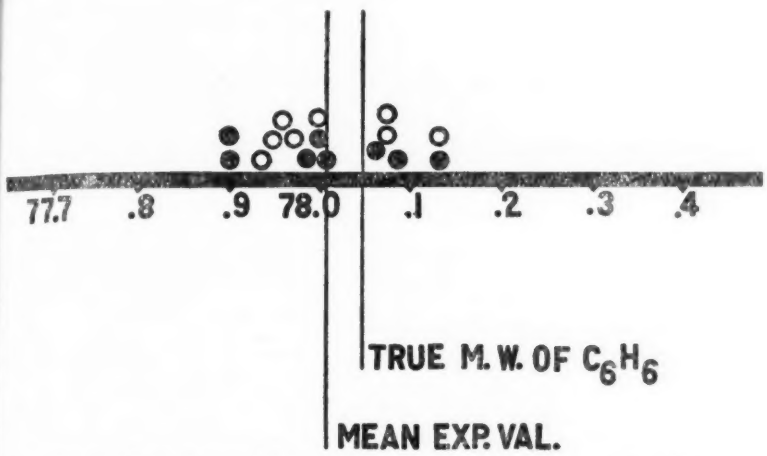

FIGURE 3.—*Plot of experimental values for the molecular weight of benzene*

The white-centered circles represent the values obtained from measurements at 0.5 atmosphere.

This research was conducted under the direction of E. W. Washburn to whom the writer is greatly indebted for guidance throughout this work.

WASHINGTON, April 25. 1930.

SEAMS FOR COPPER ROOFING

K. Hilding Beij

ABSTRACT

The various types of seams which have been proven by experience to be suitable for copper roofing are described. The ribbed or batten, the standing and the open-lock types give rise to no difficulties, if properly made, and, therefore, no tests of these seams were necessary.

While flat-lock seams calked with white lead and linseed oil have given very satisfactory service in the past, a quantitative measure of the water-tightness of these seams is desirable. Leakage tests showed that calked seams can be used wherever the depth of water which may be standing for several days on the roof will not exceed 4 inches, a depth rarely occurring except in gutters. A small section of seam removed from a roof after many years of service stood continuously for 45 days under 12 inches of water without any signs of leaking.

Tensile tests of one-half-inch flat lock and of lap seams yielded the following results:

1. Seams made with resin, killed acid, or a commercial "prepared" flux are equally strong.

2. Seams made parallel to or transverse to the direction of rolling of the copper are equally strong.

3. The strength of lap seams, one-fourth to 1 inch wide, is proportional to the width.

4. On one-half-inch flat-lock seams a large increase in the amount of solder used results in only a small increase in strength.

5. Pretinning by dipping the edges of the sheets to be joined in solder or tin increases the strength very greatly in the case of flat-lock seams.

The last two of these conclusions are of considerable importance, for it is believed by many roofers that a strong flat-lock seam can only be secured by the lavish use of solder. The tests proved, however, that the maximum strength is secured by pretinning, and large quantities of solder on the exposed surface of the seams are of little value.

The results of prolonged loading tests indicated that the maximum safe load for soldered lap seams is about 350 lbs./in.^{2} of seam and about 375 lbs./in.^{2} pretinned flat-lock seams. Under greater loads failure occurs after a time, depending on the magnitude of the load.

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V. Soldered seams
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I. INTRODUCTION

The value of a sheet-metal roof in protecting a building from the destructive agencies of the weather is dependent in great measure on

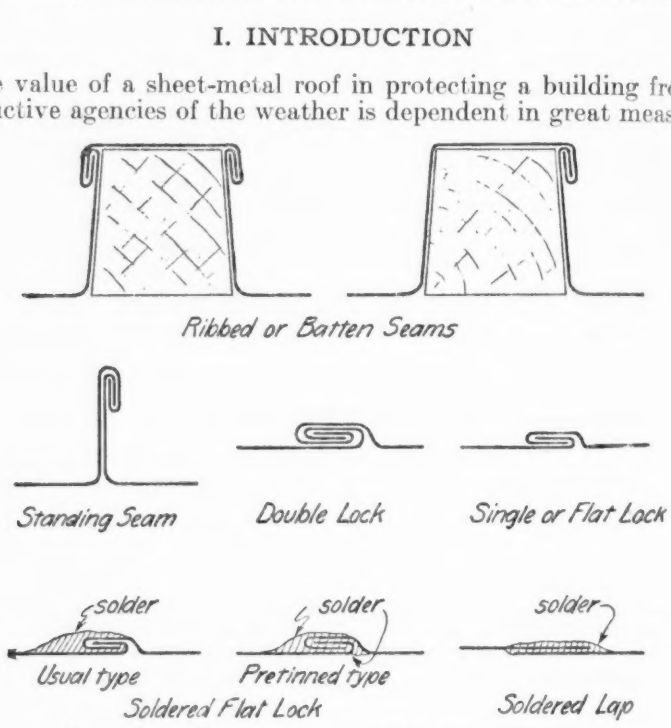

FIGURE 1.—*Types of seams suitable for copper roofing*

the character of the seams which join the sheets. With copper roofing, chosen primarily for long life, it is essential to secure durable weatherproof seams. Most of the various types of seams which experience has demonstrated to be suitable for copper roofing give uniformly satisfactory service. With some types, however, difficulties are occasionally experienced. Often these difficulties can be attributed to improper construction, but sometimes they can not be readily explained without a more complete knowledge of the properties of the seams. It is the purpose of this investigation to provide the additional data needed. The investigation is part of a study of copper

roofing problems conducted by the Copper & Brass Research Association and the National Bureau of Standards.

The seams commonly used for copper roofing are shown in Figure 1. Which type is to be chosen in any particular case depends on the design of the roof. The loosely locked types which very rarely cause trouble are suitable only for fairly steep, freely draining surfaces. On nearly level roofs and in gutters, where water may collect to an appreciable depth, either calked or soldered seams are required. If the appearance of the roof is important from the architectural standpoint, then the form and arrangement of the seams must be taken into account.

Two other considerations must always be kept in mind in any discussion of seams. First, it is essential that proper allowance be made at the seams for the expansion and contraction of the copper sheets resulting from temperature changes. Otherwise the seams may be subjected to excessive stress and injured to the extent that their resistance to the weather is destroyed. Second, some means must be provided for attaching the sheets to the supporting roof structure. Cleats, as shown in Figure 18, consisting of bent pieces of copper with one end hooked into the seam and the other end nailed to the roof, have been found to be the best means of attachment for copper roofing. Cleats improperly made or poorly placed may be the cause of damage to seams.

For reference, a comparison between the gage number and the nominal thickness of sheet copper, for the gages mentioned in this paper, is given in Table 1. The gage number is defined by the weight of the sheet in ounces per square foot. Sixteen-ounce copper is the gage most often used. Lighter gages are not satisfactory for roofing purposes.

TABLE 1.—*Gage number and thickness of sheet copper*

Gage No. (in ounces per square foot)	Nominal thickness
	Inch
14	0.0189
16	.0216
18	.0243
20	.0270

II. RIBBED AND STANDING SEAMS

Ribbed or batten seams may be made in several ways, two of which are illustrated in Figure 1. Since these seams will leak if standing under water, they can be used only on roofs of considerable pitch. To prevent interference with free drainage they are always laid in a direction perpendicular to the eaves. Ribbed seams make adequate allowance for temperature changes as the sheets are free to expand or contract slightly at the base of the ribs and also in the loose locks at the top of the ribs. This type is best suited for large structures where appearance is of great importance.

Experience has shown that ribbed seams give satisfactory service and, therefore, no tests were necessary.

The standing seam (fig. 1) is cheaper and, therefore, used more often than the ribbed seam. Like the ribbed seam, it is suitable only

for fairly steep roofs, and must be laid perpendicular to the eave. Standing seams should be neither soldered nor riveted for the additional restraints imposed are apt to result in unsightly buckling of the sheets and, in extreme cases, tearing or cracking. An example of what may happen when standing seams are riveted is shown in Figure 2.

No tests were made on standing seams, since they give rise to no troubles if made according to recommended practice.

III. FLAT SEAMS, DOUBLE AND SINGLE LOCK

The open double-lock and single-lock seams (fig. 1) are used for the cross seams between ribbed or standing seams, and, in general, on steep slopes where there must not be any obstruction to the free flow of water. Obviously, they are unsuitable for places where water may be standing on the roof because the water will gradually seep through the locks. These seams are very rarely subject to injury due to temperature changes, since there is ample allowance in the locks for slight relative movements of the adjacent sheets.

The double-lock seam is not often used, chiefly because there are six thicknesses of metal in the lock. It is therefore very difficult to secure a good joint where one seam meets another at right angles. The single lock, commonly called a flat-lock seam, is free from this objection and is also more economical of material.

No tests were made on these open-lock seams for they rarely cause any difficulties.

IV. CALKED SEAMS

A calked seam is made by coating the edges of the sheets to be joined with a thick paste of white lead and linseed oil and then forming a flat lock. If properly made, the seam is completely filled with the white lead. The practice of calking flat-lock seams was quite common 30 or 40 years ago, but has died out to a great extent at present. Possibly the laborious and dirty job of mixing the dry lead with the oil as it was required brought about the more extensive use of solder to take the place of calking. The white lead in paste form can now be purchased ready mixed, so that this objection is no longer of any moment.

Calked seams possess several advantages. They can be used on roofs of very flat slope and other places where the ordinary lock seam would leak. As compared with soldered seams they are cheaper, better in appearance, and less likely to be damaged by temperature effects because the connection between the sheets is not so rigid and a slight amount of relative movement is possible.

Although calked seams have proven successful on numerous buildings, the State House in Boston being a notable example, a need has been felt for some quantitative measure of their proof against leakage. Accordingly, tests were made to determine the head of water which a calked seam can support.

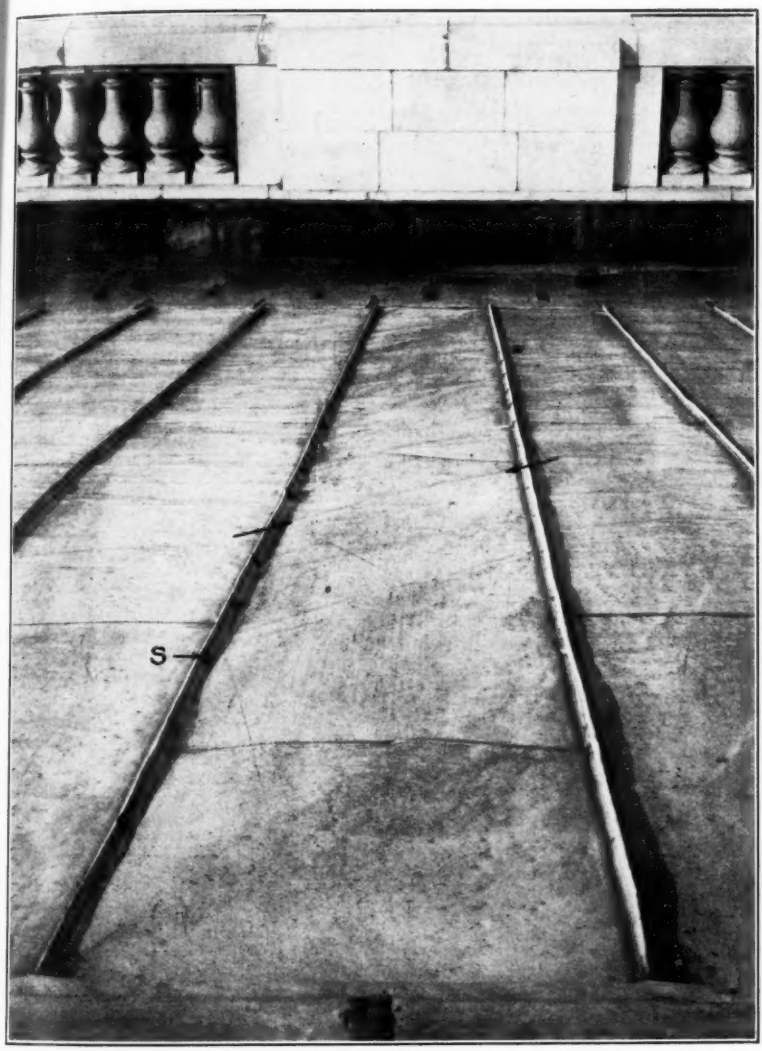

FIGURE 2.—*Diagonal buckling and tearing of copper due to riveting of standing seams*

The row of sheets in the center of the photograph lies directly over an expansion joint in the concrete roof. If there had been no rivets, a large part of the movement caused by temperature changes would have been taken up by slipping of the sheets relative to each other in the seams. This slipping was prevented by the rivets. Note the excessive buckles running diagonally across the sheets, one of which is indicated by the arrows. The copper was torn at the rivets at all the dark spots (as at *S*). These spots are patches applied to stop leaking.

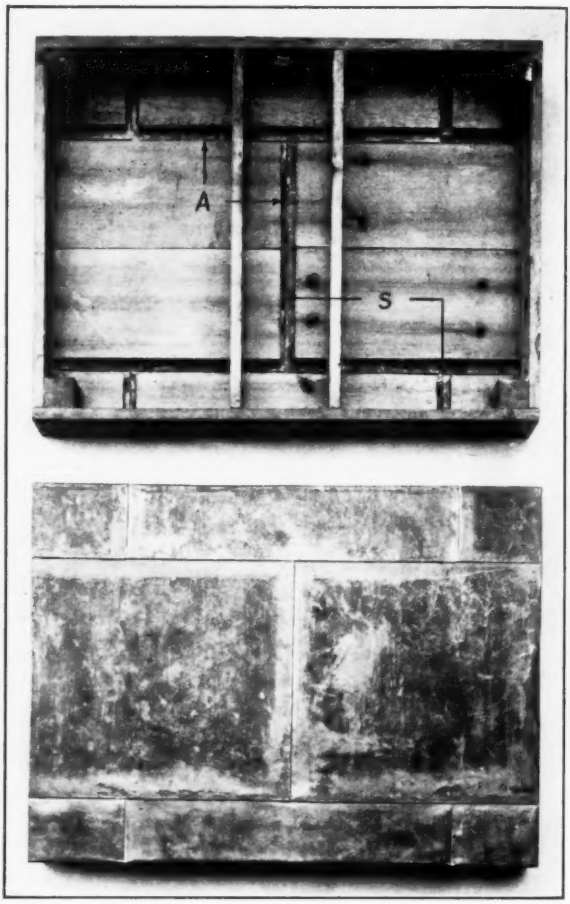

FIGURE 3.—*Roof specimens with new calked seams for leakage tests*

Upper view shows specimen from beneath. Sheathing cut away at *A* to expose lower surfaces of seams *S*. Lower view shows top of specimen.

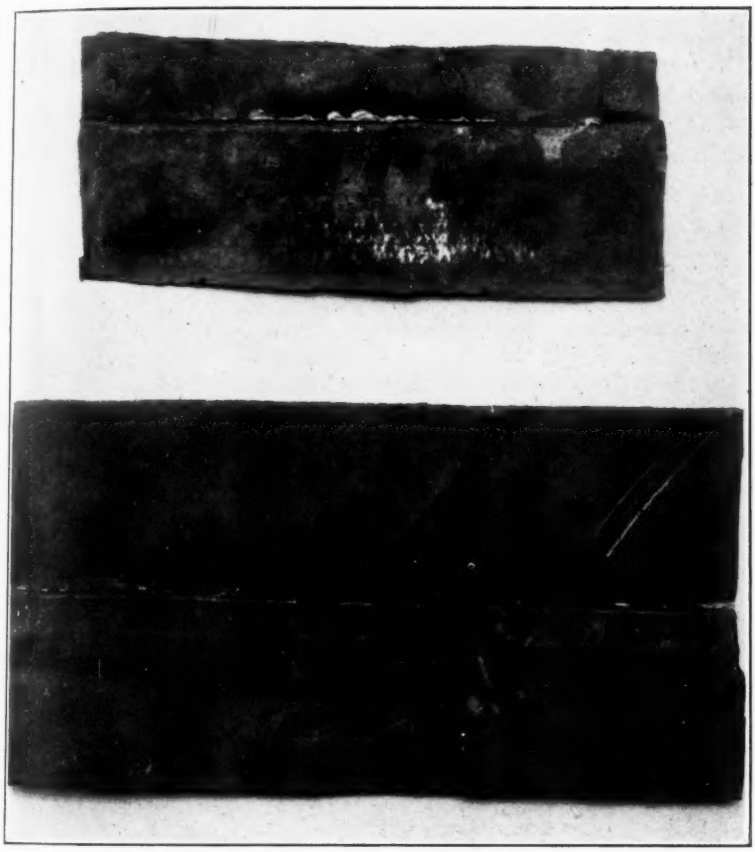

FIGURE 4.—*Sections of a calked seam removed from a building in New York City after many years of service*

Upper piece shows under surface of seam with traces of white lead near center. Lower piece shows upper (exposed) surface of seam.

1. LEAKAGE TESTS

(a) SPECIMENS

Leakage tests were made on two specimens with new seams, and on one old seam.

Two views of specimen No. 1 are shown in Figure 3. It consists of a roof section about 36 inches long by 26 inches wide covered with 16-ounce copper. The seams are half-inch flat lock calked with a white lead paste containing about 8 per cent of linseed oil. The copper was secured by cleats spaced about 9 inches apart. The sheathing under the copper was cut away, as shown at *A* on the upper view in the photograph, to expose the lower surfaces, *S*, of the seams so that any leaks might readily be observed.

Specimen No. 2 was similar in all respects to No. 1, except that the white lead paste contained about 15 per cent of linseed oil.

Specimen No. 3 was a sample selected from a number of pieces of a seam removed from a building in New York City after many years of service. Two pieces of this seam are shown in Figure 4. The smaller piece shows the appearance of the under surface of the seam; traces of the white lead can be seen at the middle of the piece. The larger section shows the upper or exposed surface. Note how inconspicuous the seam is. The sample selected for test was one which appeared to have suffered no injury during removal. The age of the seam and the composition of the white-lead mixture are not known.

Each specimen was mounted in a sheet metal tank, 13 inches deep, so that the specimen formed the bottom of the tank.

(b) TEST PROCEDURE

On the new seams, specimens No. 1 and No. 2, the order of tests was as follows: Leakage test; artificial aging; leakage test; check leakage test. On the old seam (specimen No. 3) one leakage test was made.

In the test for leakage the specimens were first subjected to a head of 1 inch of water for several days. The head was then increased at intervals of several days until leaks appeared or until the head was 12 inches.

The artificial aging process consisted of 57 cycles of alternate heating and cooling. The specimens were placed in a large heating chamber, and each morning were heated for two hours until the temperature in the chamber was about 110° F. above room temperature. The chamber was then opened and cooled to room temperature in about four hours. The specimens were again heated and left in the closed chamber to cool very slowly over night. The average temperature change for each cycle was 110° F. The maximum temperature reached was 220° F. and the minimum 70° F.

(c) RESULTS

The results of the tests are given in Tables 2, 3, and 4. In column 4 of Tables 2 and 3 wherever the rate of leakage is noted as "trace" or "slow," the leaks were so slight that they probably could not have been detected on an ordinary roof with wood sheathing. Leaks listed as "fast" would probably have been evident under similar circumstances, but in no case could they have been described as bad leaks.

Table 2 shows that only two very slight leaks appeared on each of the new specimens in a week under a head of 12 inches. This depth is far greater than any which would ever occur on a properly designed roof. In both cases these leaks were so slight that they could not have been detected in a building. In fact, on specimen No. 1 (8 per cent oil) both leaks soon disappeared and no other appeared after the fourth day.

TABLE 2.—*Leakage tests on new calked seams*

Specimen No. 1. WHITE LEAD WITH 8 PER CENT OF LINSEED OIL

Depth of water (in inches)	Total time under water	Number of leaks	Rate [1]	Location
	Days			
1	7	None.		
2	6	None.		
4	5	None.		
6	4	None.		
9	3	None.		
12	1	None.		
	2	1	Trace	Cleat.
	3	1	do	Seam junction.[2]
	4	None.		
	8	None.		

Specimen No. 2. WHITE LEAD WITH 15 PER CENT OF LINSEED OIL

1	7	None.		
2	6	None.		
4	5	None.		
6	4	None.		
9	3	None.		
12	1	1	Slow	Seam junction.
	2	2	Traces	Seam junctions.
	7	2	do	Do.

[1] Rate of leaking specified as follows: Trace, wet spot on under surface of seam; slow, water dripping at long irregular intervals; fast, water dripping steadily, less than 5-minute intervals.
[2] Seam junction refers to a place where a cross seam connects with a longitudinal seam.

TABLE 3.—*Leakage tests on new calked seams after artificial aging*

Specimen No. 1. WHITE LEAD WITH 8 PER CENT OF LINSEED OIL

Depth of water (in inches)	Total time under water	Number of leaks	Rate [1]	Location
	Days			
1	3	None.		
2	3	None.		
3	3	None.		
4	2	None.		
	3	1	Trace	Cleat.
	4	1	Slow	Do.
	5	1	Trace	Do.

[1] Rate of leaking specified as follows: Trace, wet spot on under surface of seam; slow, water dripping at long irregular intervals; fast, water dripping steadily, less than 5-minute intervals.

TABLE 3.—*Leakage tests on new calked seams after artificial aging*—Continued

SPECIMEN DRIED FOR ONE WEEK AND RETESTED

Depth of water (in inches)	Total time under water	Number of leaks	Rate	Location
	Days			
1	7	None.		
2	5	None.		
3	7	None.		
4	11	None.		
5	[2] 0	1	Slow	Cleat.
	5	1	Trace	Do.
	14	3	Traces	Do.
	18	3	do	Do.
6	4	3	do	Do.

Specimen No. 2. WHITE LEAD WITH 15 PER CENT OF LINSEED OIL

1	3	None.		
2	[2] 0	1	Trace	Cleat.
	2	2	Traces	Cleats.
	3	3	do	Do.
	5	2	do	Do.
	9	None.		
	11	1	Trace	Cleat.
		1	do	Seam junction.

SPECIMEN DRIED FOR ONE WEEK AND RETESTED

1	7	None.		
2	2	None.		
	3	1	Trace	Cleat.
	14	1	do	Do.
		1	do	Seam junction.
3	18	1	do	Cleat.
		1	do	Seam junction.
4	3	1	do	Cleat.
		1	do	Seam junction.
	4	4	Traces	Cleats.
		1	Fast	Cleat.

[2] 1 hour.

TABLE 4.—*Leakage test on old weathered calked seam*

SPECIMEN NO. 3

Depth of water (in inches)	Total time under water	Number of leaks	Depth of water (in inches)	Total time under water	Number of leaks
	Days			*Days*	
1	14	None.	5	18	None.
2	5	None.	6	31	None.
3	7	None.	7	31	None.
4	11	None.	12	45	None.

During the tests, some of the white lead leached out of the seams on both specimens Nos. 1 and 2 in the form of a fine, white powder. The relative amounts of the sediment on the two specimens could not be accurately measured, but it was quite evident by inspection that less powder was formed on specimen No. 1. This would indicate a slight superiority of the white-lead paste with 8 per cent of linseed oil.

The only visible effects of the artificial aging process were the discoloration of the white lead, which turned a light yellow color, dark-

ening to brown in patches, and a few very small surface cracks in the white lead. Otherwise the seams appeared to be unchanged, and there was no appreciable buckling or other distortion of the copper sheets.

However, the aging greatly impaired the water-tightness as is evident in Table 3. In the first test after aging, on specimen No. 1, 8 per cent oil, one slight leak appeared under 4 inches of water; and on specimen No. 2, 15 per cent oil, three slight leaks under 2 inches of water. After this test the specimens were dried in the laboratory for one week, and then retested. Specimen No. 1, this time developed only three slight leaks during 18 days under 5 inches of water. These leaks did not increase in four days under 6 inches of water. On specimen No. 2 five leaks developed in four days under 4 inches of water. One of these probably would have been sufficient to penetrate any ordinary roof sheathing. These tests show that the white lead paste with 8 per cent of linseed oil, as used on specimen No. 1, is definitely superior to that with 15 per cent of linseed oil.

It should be noted that all of the leaks occurred either at cleats or at seam junctions; that is, places where the cross and longitudinal seams meet.

The artificial aging can not, of course, be considered as directly comparable with the aging which takes place on a roof. In one respect the test was more severe than actual service conditions for the high temperatures were 50° to 70° F., higher than any which would ever occure on a roof. Nevertheless, even after this severe treatment, the seams calked with white lead paste containing 8 per cent linseed oil were still satisfactory, for only under very extreme conditions would water on a roof be likely to reach a depth of 4 inches.

The tests of the old weathered seam, specimen No. 3, Table 4, were surprising in that no trace of a leak could be detected even after 45 days under a head of 12 inches of water. The results indicate that long service is not likely to impair the water-tightness of calked seams. It is possible, however, that if the specimen had been large enough to include a seam junction or a cleat, some slight leakage might have occurred at these places.

It may be concluded that seams calked with white lead with 8 per cent of linseed oil will give satisfactory service wherever the depth of water standing on the roof for several days will not exceed 4 inches. There is little likelihood that the seams will leak under depths 2 or 3 inches greater, provided the water drains off in a few hours.

V. SOLDERED SEAMS

Soldered seams (fig. 1) are intended for roofs of very slight slope, for gutters, and, in general, for places which may be flooded with water. The soldered flat lock is the more common form, as it permits the use of cleats for fastenings. The lap seam is used where cleats are not needed or where it may be difficult to make a flat lock.

Proper allowance for the effects of temperature changes is more difficult to secure with soldered seams than with other types, as there can be no relative movement in the seams between the adjacent sheets. Adequate roof fastenings, carefully placed, are essential for best results, and special expansion joints are sometimes desirable. The seams themselves must be strong enough to withstand the stresses caused by temperature changes. When failure occurs, it is generally

due to insufficient strength of the seams; the solder cracks and the roof begins to leak.

1. TENSILE TESTS

The purpose of the tensile tests was to determine the influence of various factors on the strength of soldered seams. The factors taken into consideration were: (1) The kind of flux; (2) the direction of rolling of the copper, (3) the width of lap seams; (4) the width (amount) of solder on flat-lock seams, and (5) pretinning. The effects of variations in the composition of the solder and in the quality of the workmanship were not studied.

(a) SPECIMENS

The tensile specimens consisted of eight sets such as that given in Table 5.

TABLE 5.—*Set of specimens for tensile tests of soldered seams*

[Two sets of specimens, one with seams parallel and one with seams transverse to the direction of rolling of the copper, were made from each of four gages of copper, namely, 14, 16, 18, and 20 ounces]

LAP SEAMS

Flux	Pretinning	Widths of seam tested	Number of specimens
		Inch	
Resin	None	¼, ½, ¾, 1	16
Acid	do	¼, ½, ¾, 1	16
Prepared	do	¼, ½, ¾, 1	16
Acid	With solder	¾	4
	With tin	¾	4

FLAT-LOCK SEAMS

Flux	Pretinning	Widths of seam tested	Widths of solder [1] tested	Number of specimens
		Inch	*Inches*	
Resin	None	½	½, 1, 2	12
Acid	do	½	½, 1, 2	12
Prepared	do	½	½, 1, 2	12
Acid	With solder	½	1	4
	With tin	½	1	4

Total number of specimens in set, 100.

[1] Width of band of solder showing on finished seam. This width is taken as a measure of the amount of solder used.

The quantities of solder corresponding to the different widths as given in the fourth column of the second part of Table 5 were determined by weighing representative specimens and deducting the estimated weight of the copper. The values thus obtained seemed so low that they were checked by weighing specimens before and after burning off the solder, and also by weighing the solder scraped from specimens. The results, which checked reasonably well, are given in Table 6. There were variations of as much as 50 per cent from specimen to specimen.

TABLE 6.—*Amount of solder on flat-lock seams*

Width of solder band (in inches)	½	1	2
Amount of solder (in ounces per lineal inch of seam)	0.04	0.06	0.21

Sample seams were made in lengths of 8 inches joining sheets of copper about 6 inches wide. The joined sheets were cut into four specimens each 2 inches wide with the seams crossing the middle of the specimens. From these, tensile specimens were prepared with a reduced width of 1¼ inches over a gage length of 4 inches. All soldering was done by the same man under conditions as nearly similar as possible. No laboratory refinements of any sort were used. The work was of uniformly high quality such as would be found on the best of copper roofs.

Pretinning was done as follows: Solder, or tin, was melted in containers of the requisite size heated by gas. The copper sheets were dipped into killed acid flux to a depth of 1½ inches. While still wet with the flux, the sheets were dipped into the molten solder, or tin, quickly removed, wiped clean with a cloth, and then allowed to cool. Temperatures were not measured. This procedure is in accord with shop practice.

All other specimens were tinned with solder flowed on with a soldering copper, just as would be done on a roofing job.

Commercial roofing-temper, soft copper was used. This was electrolytic copper, 99.953 per cent copper by analysis, with no unduly large proportion of any impurity. The solder and tin were purchased in the open market. The solder analyzed 48.8 per cent tin and 50.8 per cent lead; and the tin 99.1 per cent tin.

The acid flux was made up in the usual way from clean zinc scraps and hydrochloric acid. Great care was taken to "kill" the acid thoroughly. Even so, analysis showed 5.2 per cent free hydrochloric acid in the resulting flux. The "prepared" flux was a commercial article containing about 86 per cent zinc chloride and about 12 per cent ammonium chloride.

Eight tensile specimens of 0.75-inch width and 4-inch gage length were prepared from each gage of copper.

(b) TEST PROCEDURE

The tests were made in the usual manner on a 20,000-pound testing machine with a counterpoise giving a range of 5,000 pounds.

(c) RESULTS

The tensile strength of the sheet copper was determined for purposes of comparison. The results are given in Table 7, and are shown by broken lines on the graphs in Figures 5 to 12, inclusive.

TABLE 7.—*Tensile strength of sheet copper*

Gage of sheet (in ounces per square feet)	Nominal thickness	Number of specimens	Average tensile strength	Maximum deviation from average
	Inch		*Lbs./in.²*	*Per cent*
14	0.0189	8	31,300	4.2
16	.0216	8	31,900	1.9
18	.0243	8	32,100	2.2
20	.0270	8	32,200	1.9

1. FLUX.—In Figures 5 to 8, inclusive, each graph shows the comparative tensile strengths of specimens made with resin (circles), killed acid (squares), and "prepared" flux (triangles), with seams parallel and transverse to the direction of rolling. The markedly low values of occasional points on the graphs are due to seams with imperfections in soldering, such as bubbles, untinned spots, etc.

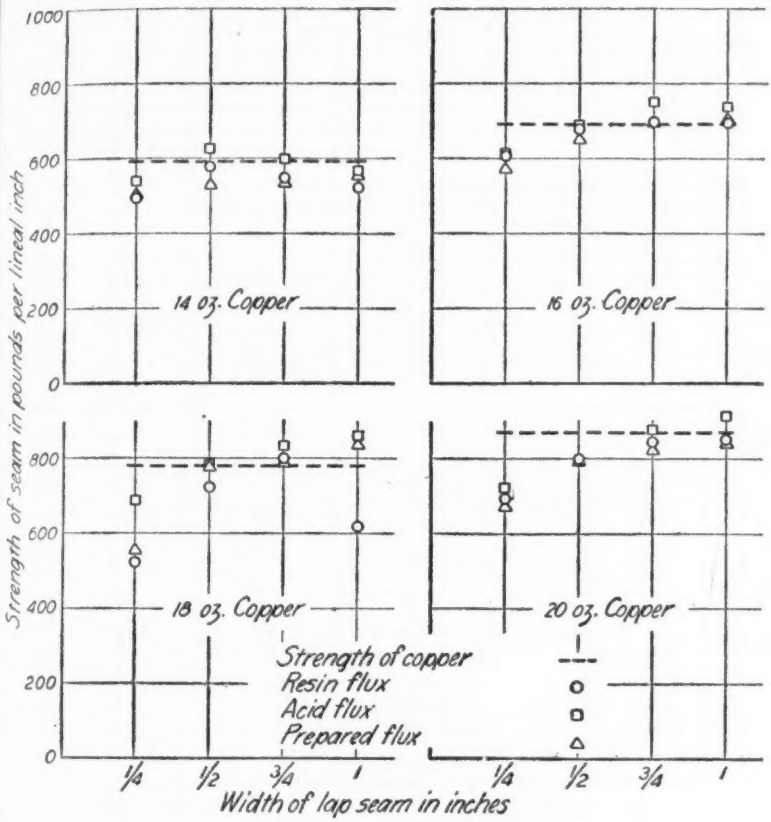

FIGURE 5.—*Effect of flux on strength of lap seams*

Seams parallel to the direction of rolling of the copper. Each point is an average for four specimens

There are no differences in the tensile strengths of either the lap seams or the flat-lock seams which can be ascribed to the kind of flux used. It should not be assumed, however, on the basis of this conclusion, that all fluxes are equally satisfactory. All traces of flux can not be removed from the seams after a roof is completed. If the flux is corrosive, there is a possibility that corrosion may be started which otherwise would not occur. Since equally strong seams result from the several kinds of flux tried, it is reasonable to infer that the flux which is least corrosive will give the most satisfaction in service.

2. DIRECTION OF ROLLING.—As no difference in strength depending on the flux was found, the results for all three fluxes on each type and size of seam were averaged. The average values are plotted on the graphs in Figures 9 and 10 to show any relation which might exist between the direction of rolling of the copper and the strength of the seams. It is evident from the graphs that seams parallel and transverse to the direction of rolling are equally strong.

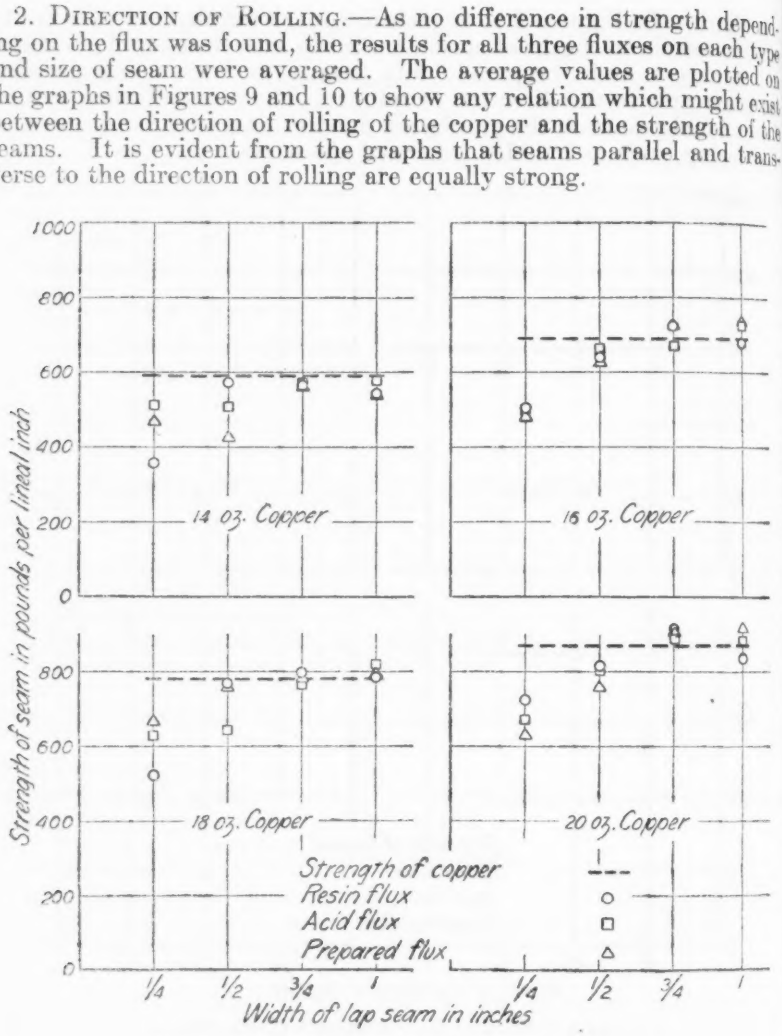

FIGURE 6.—*Effect of flux on strength of lap seams*

Seams transverse to the direction of rolling of the copper. Each point is an average for four specimens

3. WIDTH OF LAP SEAMS.—In Figure 11 the graphs show the relation between the strength and the width of lap seams. Each point represents the average strength of a given width of seam on one gage of copper, including seams both parallel and transverse to the direction of rolling and made with the three kinds of flux.

Specimens with seams which were not as strong as the copper broke in the seams. The results for these can be closely approximated on each graph by a sloping straight line, showing that the strength of the seams increases in proportion to the increase in width of seam. As

nearly as can be judged, the strength increases at the same rate on all thicknesses of copper which were tested.

Above a certain critical width the seam strengths are practically constant, as shown by the continuous horizontal lines on each graph. Some of the specimens of seams at approximately this critical width broke in the seam and others in the sheet copper itself. Seams of greater width (1 inch) nearly all broke in the copper. The results for seams wider than the critical width, therefore, ought to correspond

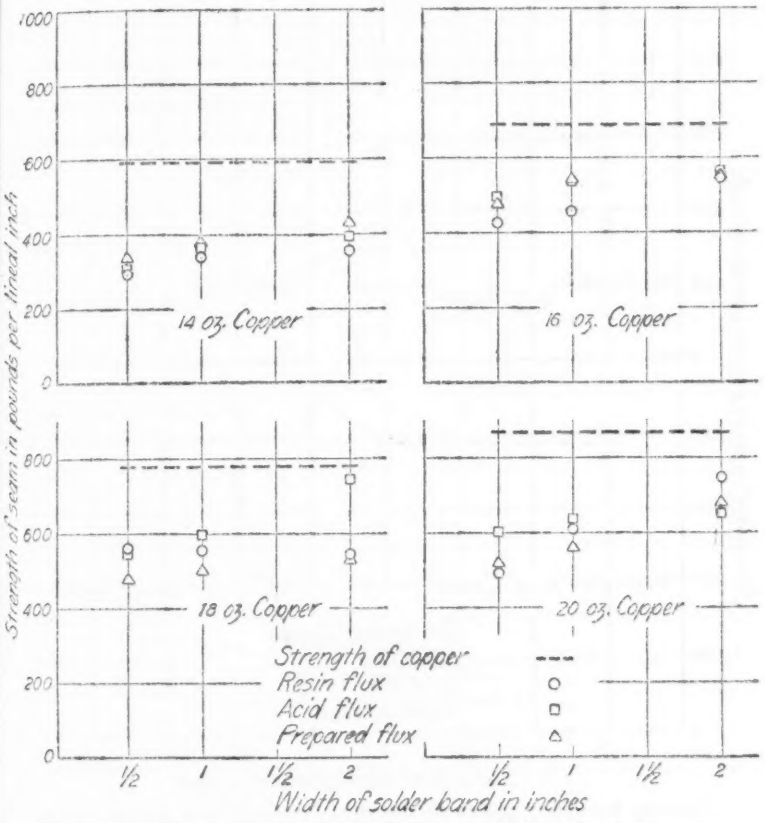

FIGURE 7.—*Effect of flux on strength of one-half inch flat-lock seams*

Seams parallel to the direction of rolling of the copper. Each point is an average for four specimens

very closely to the results for sheet copper represented by the broken horizontal lines. The graphs show that they do so. The greatest discrepancy occurs on the 14-ounce copper where the maximum strength of the seams is about 7 per cent less than the strength of the copper sheet. On the 16-ounce copper the discrepancy is about 3 per cent and on the other two gages less than 1 per cent, the seam strength being greater than that of the copper in each case. These discrepancies are probably due to variations in the copper sheets.

It would appear that the critical width, thus determined, would be the width required for roofing seams. This is not the case, as will be brought out later in the discussion of the prolonged loading tests, for the total time during which a seam is under load must also be considered. The results of the tensile tests do show, however, that lap seams less than three-fourths inch wide will under no circumstances be satisfactory for copper roofing.

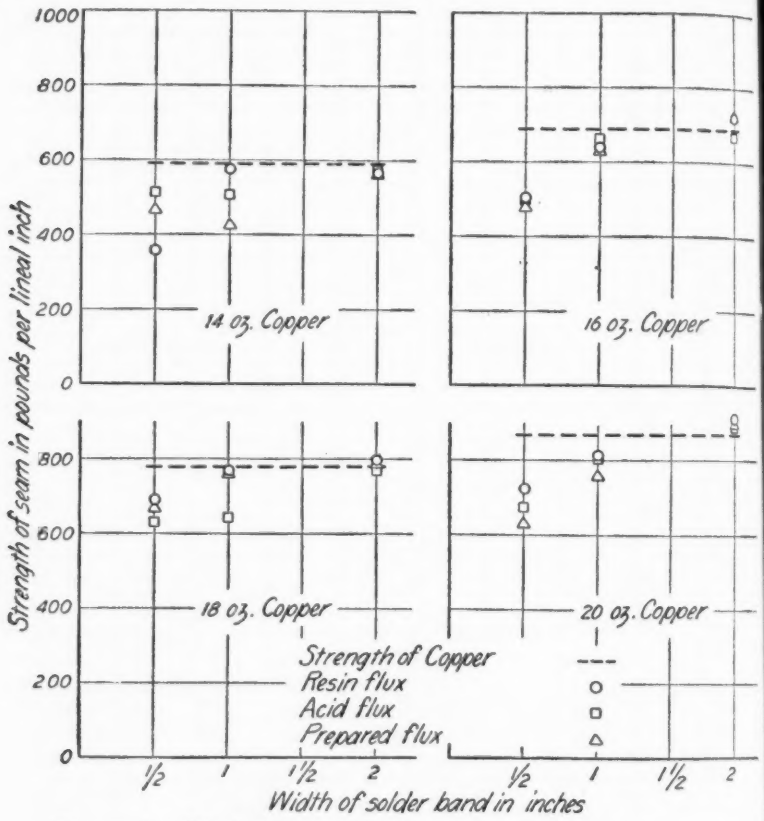

FIGURE 8.—*Effect of flux on strength of one-half inch flat-lock seams*

Seams transverse to the direction of rolling of the copper. Each point is an average for four specimens

4. WIDTH (AMOUNT) OF SOLDER, FLAT-LOCK SEAMS.—In Figure 12 the graphs show the relation between the strength of flat-lock seams and the width of the solder band showing on the finished seams. Note that a large increase in the width of the solder band, corresponding to a great increase in the amount of solder used, results in only a small increase in strength. Also note that even with the greatest widths (largest amounts) of solder, these seams do not

pproach the strength of the copper sheets, shown by the horizontal roken lines. Evidently piling up heavy wide bands of solder on at-lock seams to increase their strength is not worth while. A ore efficient method is discussed later in connection with pretinning.

5. PRETINNING.—The strengths of lap and flat-lock seams pre-nned with "50–50" solder (half lead, half tin) as compared with ose pretinned with tin are shown in the graphs of Figure 13. The retinning is equally effective whether solder or tin is used.

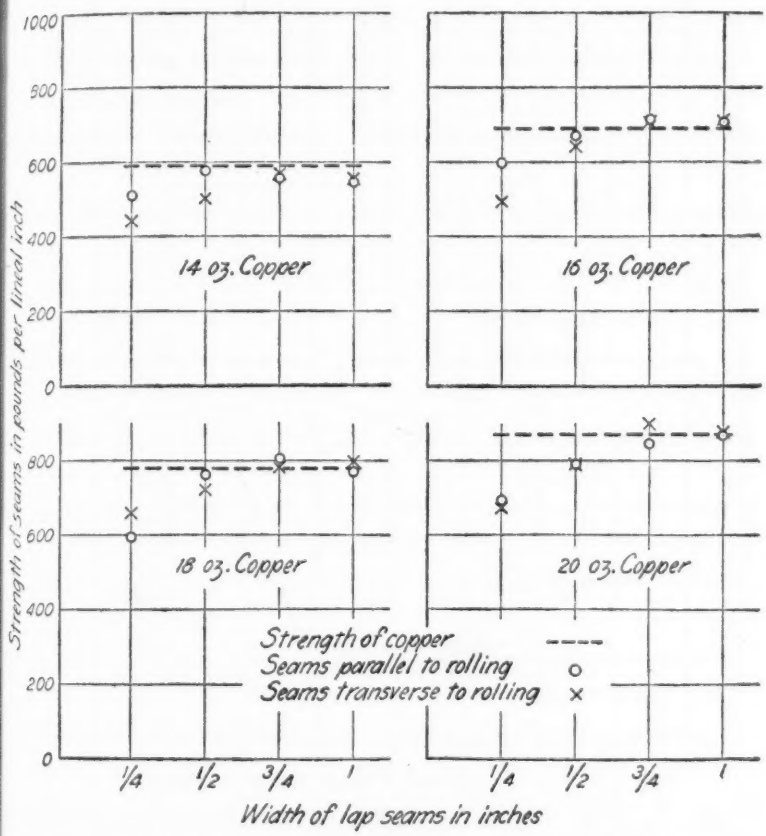

FIGURE 9.—*Effect of direction of rolling of copper on strength of lap seams*
Each point is an average for 12 specimens

As the three-fourths-inch lap seams, whether pretinned or not, are pproximately equal in strength to the copper sheets of all gages ested (fig. 11), the effect of pretinning can not be shown graphically. owever, 30 per cent of the specimens not pretinned and only 11 er cent of the pretinned specimens failed in the seam, indicating hat the pretinning does result in greater strength. The increased trength is due to the greater uniformity and the more thorough nion of solder, or tin, to copper obtainable by pretinning.

On the flat-lock seams a very great increase in strength result from pretinning, as shown in Figure 14. With pretinning it is possible to obtain complete union between all the layers of copper in the seam, whereas in the flat-lock seam as ordinarily made without pretinning only two of the layers are completely joined. See Figure 1. There is a decided falling off of the strength of the pretinned seams on the 20-ounce copper. Examination of these specimens

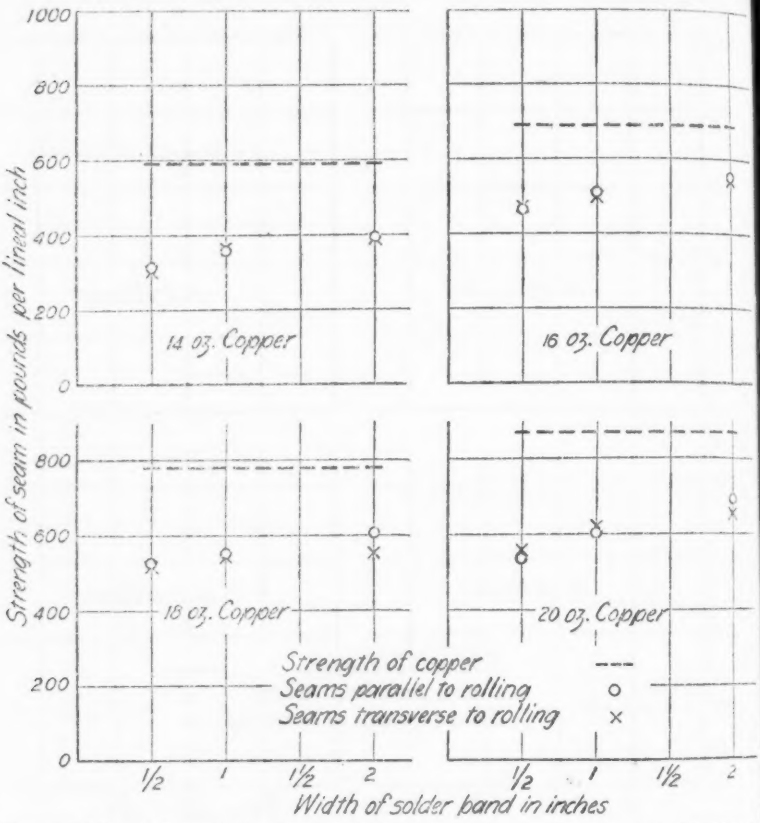

FIGURE 10.—*Effect of direction of rolling of copper on strength of one-half inch flat-lock seams*

Each point is an average for 12 specimens

disclosed incomplete joining of the solder. In all probability because of the greater thickness of these seams, enough heat was not supplied by the soldering copper to melt or "flow" the solder.

These results are of great importance as concerns copper roofing. Soldered flat-lock seams are practically always used for flat roofs and gutters, and usually they are not pretinned. These seams probably give more trouble than all other types combined. Pretinning, even if it will not completely solve the problem, very likely

will eliminate most of the trouble. The main point is that lock seams which are completely filled with solder are much stronger than those made in any other way.

2. PROLONGED LOADING TESTS

It has been observed that cracks sometimes appear in the solder of seams which have been perfectly satisfactory for one or more years.

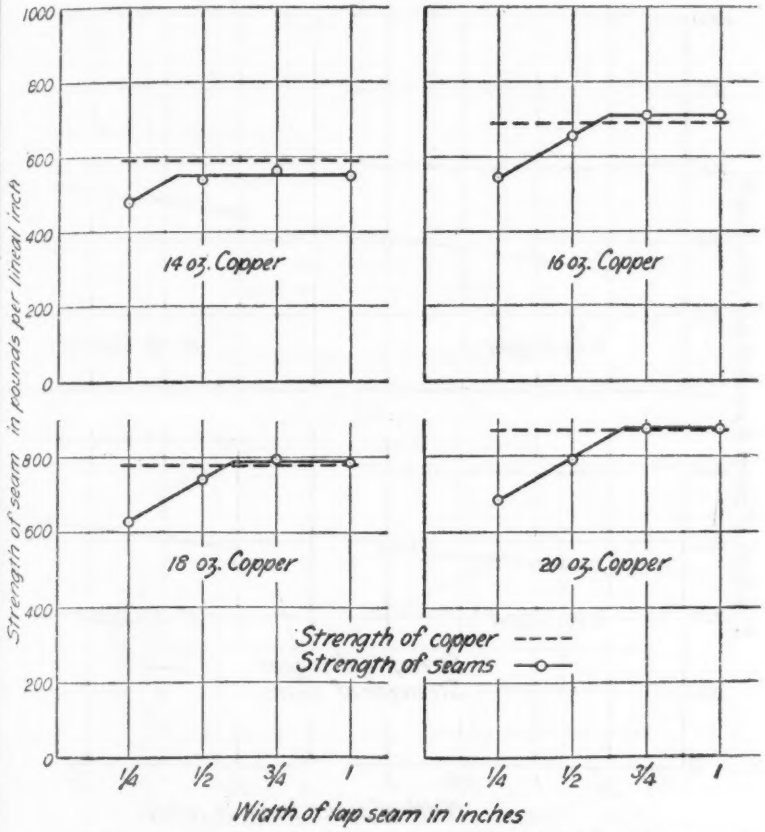

FIGURE 11.—*Effect of width of lap on strength of lap seams*

Each point is an average for 24 specimens

The results of the short-time tensile tests furnish no clue to this behavior of seams. However, it has long been known that solder will flow or "creep" under the continued action of a load not large enough to cause immediate failure. If the load is sufficiently large, the flow will continue until the solder fails. Solder in a joint or seam behaves in a similar manner. Previous work [1] has been concerned with

[1] See, for example, "Tensile Properties of Soldered Joints under Prolonged Stress," Freeman and Quick, The Metal Ind., N. Y.; January, 1926.

specially prepared specimens not at all representative of seams such as would be found in a copper roof. The tests to be described were undertaken in order to obtain data on seams made according to roofing practice.

(a) SPECIMENS

The specimens consisted of copper strips 2 inches wide and 12 inches long with a transverse seam at the center. For the one-fourth and one-half inch lap seams, the full width specimens were tested. All

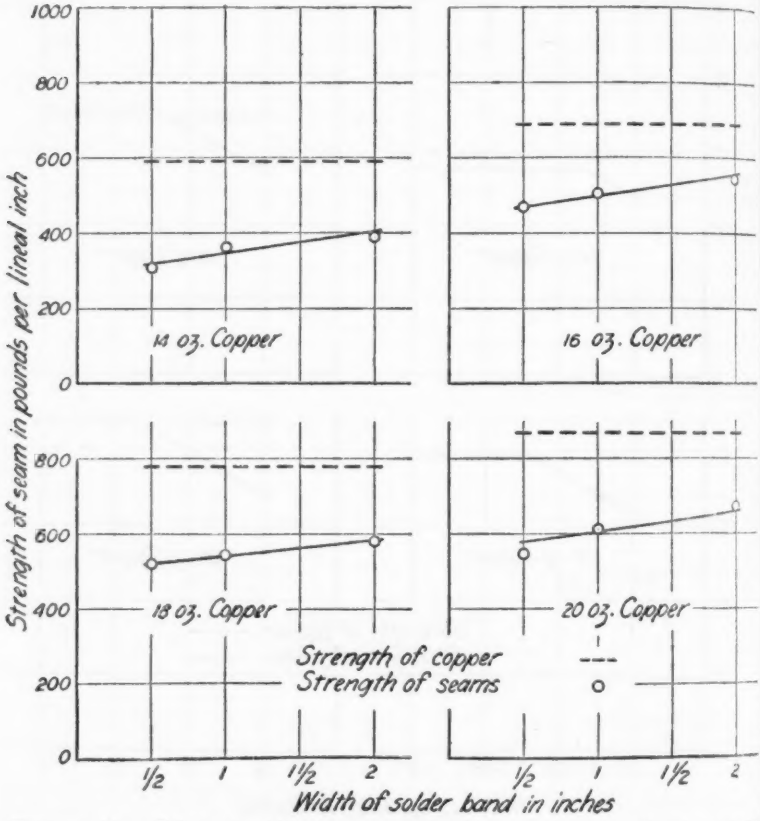

FIGURE 12.—*Effect of width (amount) of solder on the strength of one-half inch flat-lock seams*

Each point is an average for 24 specimens

others were milled down to a width of 1 inch so that smaller test loads could be used. The lap seams were made from the same materials and by the same workman as the tensile-test specimens, previously described. The flat-lock seams were made up especially for these tests. The sheet copper was from the same source as the tensile specimens. The solder was "50–50" lead-tin composition of ordinary market grade. The flat-lock seams were pretinned so that each seam was entirely filled with solder. It was not thought worth while

test flat-lock seams which had not been pretinned, since such seams ve very low strengths in the tensile tests.

(b) TEST PROCEDURE

Figure 15 is a photograph of a seam under test showing the method suspending and loading the specimen. Each specimen was in-

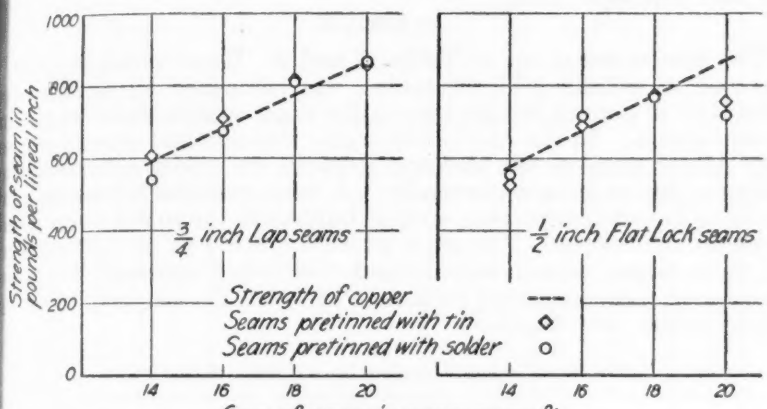

FIGURE 13.—*Comparsion of results of pretinning with tin and with "50–50" (half lead, half tin) solder*

Each point is an average for 8 specimens

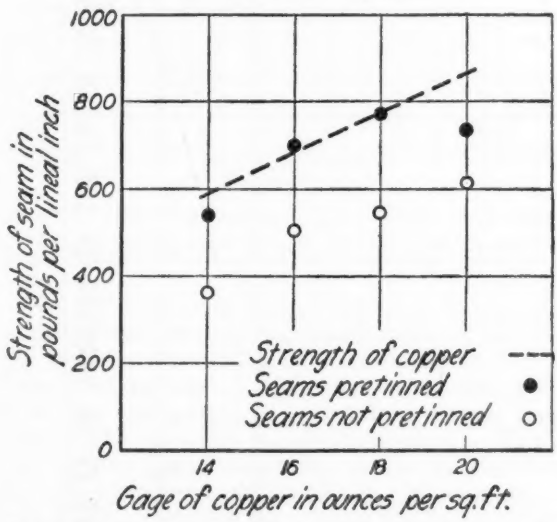

FIGURE 14.—*Effect of pretinning on strength of one-half inch flat-lock seams*

Each point is an average for 16 specimens

spected morning and evening so that the time of failure was deter-mined within half a day. The specimens under very heavy loads were inspected hourly during the first 10 hours.

"Creep" was not measured. It was observed, however, that failure occurred in a progressive manner. On both types of seams the first

indications of failure were fine cracks in the solder along the edges of the seams. These cracks gradually opened and spread toward the center of the seam until finally the solder gave way suddenly. On the lap seams with the heaviest loads this progressive failure took place within a half hour, while on one or two of the flat-lock seams under light loading the initial crack was observed nearly two weeks before the final complete failure.

(c) RESULTS

The results are given in Tables 8 and 9. The "nominal stress," reported in column 3 of the tables, was computed by dividing the total load in pounds by the area of the seam (width times length) in square inches. In the case of lap seams this nominal stress becomes very nearly equal to the shearing stress in the solder as soon as the solder begins to deform plastically. A number of the lap seams were found to have imperfections, such as bubbles in the solder or untinned spots on the copper. The areas which appeared to be well soldered on these seams were measured and "corrected stresses" based on these areas were computed (column 4 in Table 8). In most cases the imperfections were slight.

TABLE 8.—*Prolonged loading tests of soldered lap seams*

Gage of copper (in ounces per square foot)	Width of seam (inches)	Nominal stress [1] (lbs./in. [2])	Corrected stress [2] (lbs./in. [2])	Time to failure (days)
14	¼	1,200		0.2
		1,000		.3
		800		1.3
		700		2.1
		600		3.5
		500		6.0
		450		14.0
		410	630	2.7
		400	460	10.0
		370		86.0
	½	600	620	1.7
		500		12.0
		400		29.0
	¾	500		11.0
		400		24.0
16	¼	600		4.0
		500		10.0
		420	460	13.5
		420		21.0
		400		43.0
		380		28.0
		380		85.0
18	¼	600	680	1.0
		360		65.0
	½	600	620	4.0
		500		15.0
	¾	600	710	4.0
		500		31.0
	1	600	610	2.0
		500		10.0
		400		41.0
20	¼	600		0.0

[1] Total load in pounds divided by area of seam in square inches.

[2] On defective seams, a "corrected stress" was computed as the total load in pounds divided by the area in square inches of that part of the seam which appeared to be well soldered.

TABLE 9.—*Prolonged loading tests of one-half inch soldered flat-lock seams*

Gage of copper (in ounces per square foot)	Nominal stress [1] (lbs./in.²)	Time to failure (days)
16	900	0.5
	700	2.0
	600	3.0
	500	25.0
	450	15.0
	400	240.0
	390	231.0

[1] Total load in pounds divided by area of seam in square inches.

The data for the lap seams are plotted on the graph in Figure 16. For defective seams only the corrected values are plotted. (Open

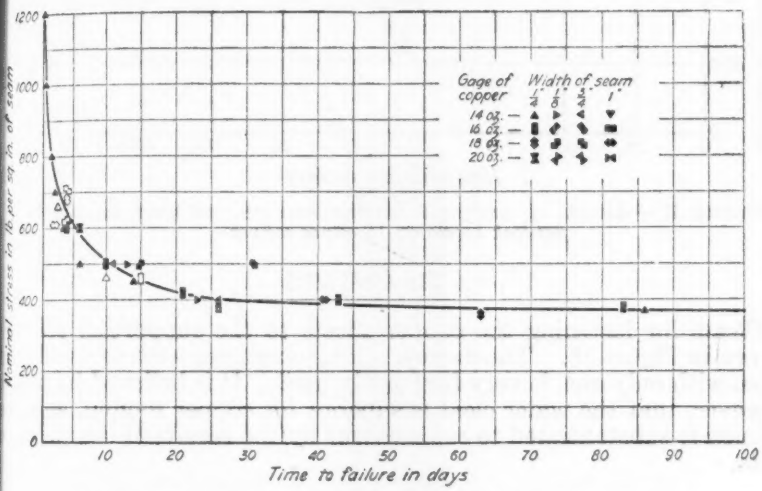

FIGURE 16.—*Results of prolonged loading tests on lap seams*

For seams with imperfect soldering corrected values were computed and then plotted in the diagram as open characters. For these seams only the corrected values were plotted

characters). No differences in the results due to variations in the gage of the copper from 14-ounce (0.0189 inch) to 20-ounce (0.0270 inch) or due to variations in width from one-quarter to 1 inch can be detected. Note that as the stress is decreased slightly under 400 lbs./in.² of seam, the time required to produce failure increases very rapidly and the curve becomes nearly horizontal. The indications are that the maximum stress which lap seams will withstand indefinitely is in the neighborhood of 350 lbs./in.² of seam.

The graph in Figure 17 gives the results for flat-rock seams. The curve is similar to that for lap seams in Figure 16, but approaches the horizontal at a slightly higher stress. The curve indicates that the maximum stress for which one-half-inch, pretinned, flat-lock seams will withstand for a very long time is about 375 lbs./in.² of seam. Flat-lock seams of other widths were not tested, but very likely these results are applicable to seams of widths up to 1 inch, at least.

The values given above may be used to determine the width of seam required if the load on the seam is known. However, a liberal factor of safety should always be used because it is not possible to determine by inspection whether or not there are any small imperfections in the soldering.

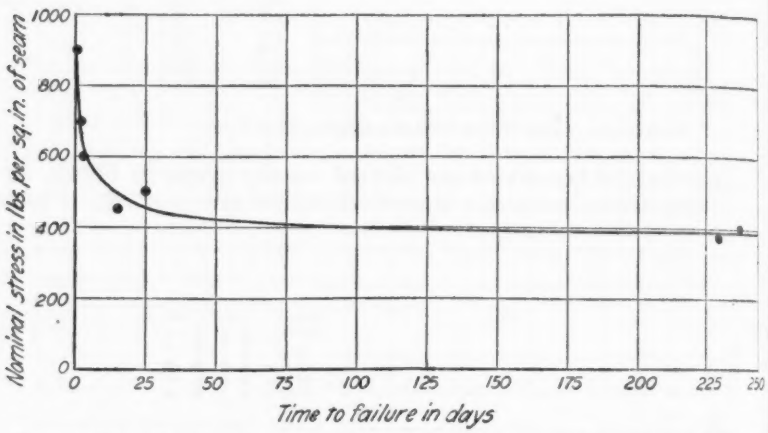

FIGURE 17.—*Results of prolonged loading tests on pretinned one-half-inch flat-lock seams on 16-ounce copper*

VI. CLEATS

Cleats for fastening the copper sheets to the supporting roof are shown in Figure 18. The narrow cleat, sometimes with two nails and often with only one, is very frequently used. It is believed by many, however, that the wider cleat is superior for copper roofing, and this opinion is substantiated to some extent by the results of comparative tests.

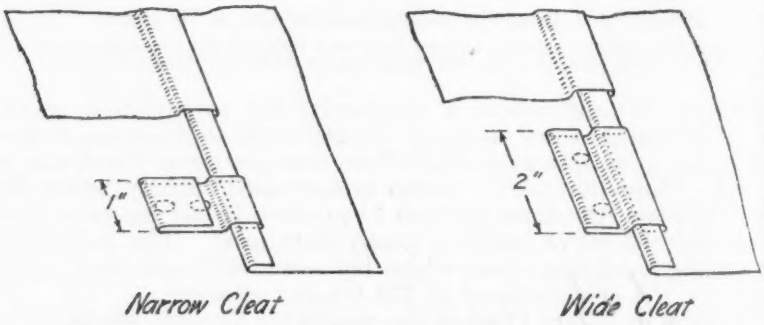

FIGURE 18.—*Cleats for fastening copper sheets to roof sheathing*

During the course of some expansion tests on a molded copper gutter 50 feet long, several methods of fastening the gutter were studied. Continuous measurements of copper roof temperatures at Washington, D. C., over the period of one year indicated that the maximum range of temperatures ever likely to occur in Washington is approximately from −20° to +160°F. The temperature range

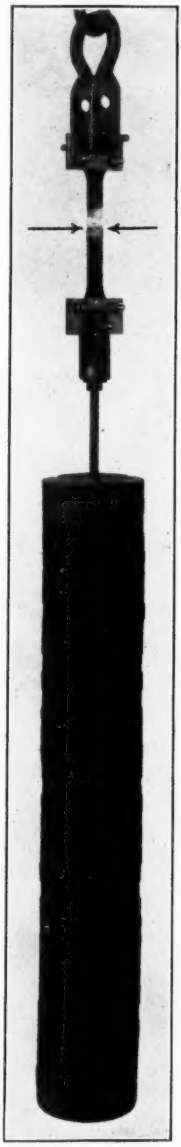

FIGURE 15.—*Prolonged loading test on pretinned ½-inch flat-lock seam*

Seam is indicated by the arrows.

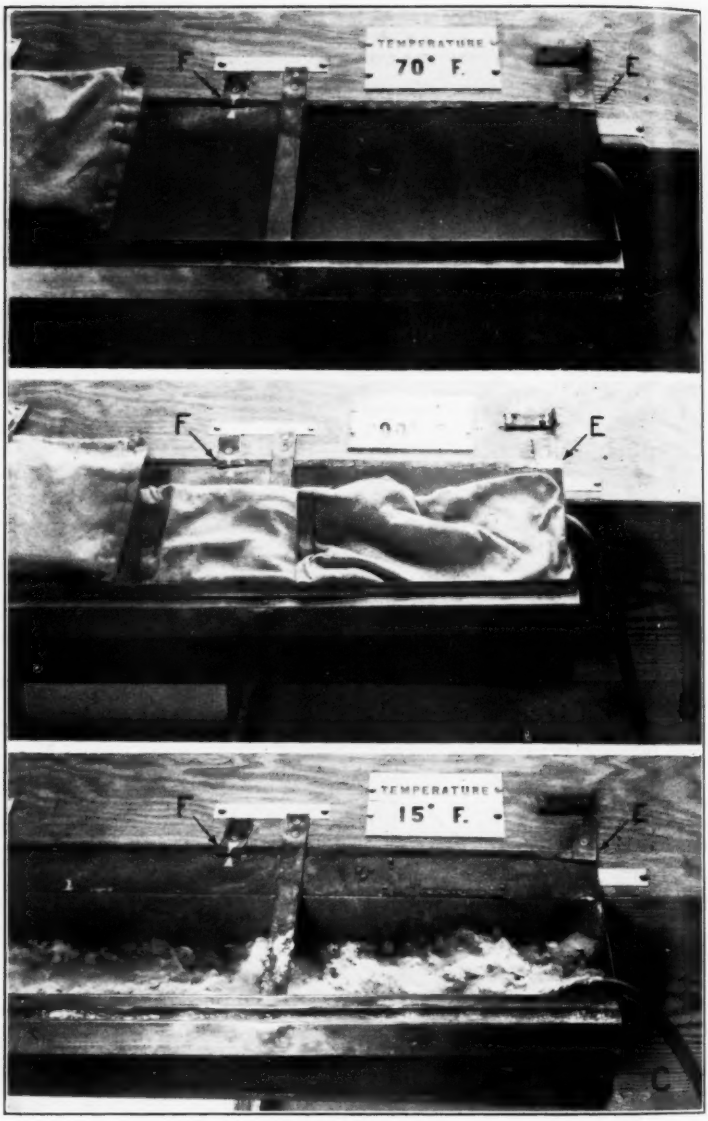

FIGURE 19.—*Tests on copper gutter fastened to sheathing with narrow cleats, one nail in each cleat*

A, Gutter at temperature of 70° F. ready for tests. Note relative positions of cleats and gutter at *E* and *F*. *B*, gutter at 200° F. Note that cleats at *E* and *F* have been displaced as gutter expanded toward the right. *C*, gutter at 15° F. Note displacement of cleats at *E* and *F* toward left due to contraction of gutter. (The pieces of fiber board and the sand bags shown in photographs *A* and *B* were used for preventing the loss of the steam which was employed for heating. Steam was supplied through a perforated pipe lying in the bottom of the gutter. Sand bags were also used to equalize the load supported by the gutter, the load being maintained practically constant throughout the test.)

the tests was about the same in extent, but for convenience was ised 35° or 40° F.

Figure 19, *A*, shows the end of the copper gutter mounted for test a temperature of 70° F. Note that the edge of the end cleat, at *E*, flush with the end of the gutter, and the painted marker on the cond cleat from the end, at *F*, points directly to the marker painted the gutter itself. Figure 19, *B*, shows the gutter heated by steam a temperature of about 200° F. The end of the gutter (*E*) has oved one-quarter inch or more toward the right. (The other end oved an equal distance toward the left.) As the gutter expanded, e friction between the cleats and the gutter was great enough to splace the cleats, as shown in the photograph. Note particularly w the marker on the second cleat at *F* points diagonally toward e right. Similar movements, in the opposite direction, took place hen the gutter was cooled to 15° F. by means of cracked ice and lt. See Figure 19, *C*, at *E* and *F*. It is obvious that any con-nued action such as this, even if less pronounced, would eventually sult in damage to the cleat, probably by tearing at the nail. When eats of the same dimensions, but with a second nail placed an inch yond the first in the center-line of the cleat were tested, their dis-acement as the gutter expanded and contracted was much less pro-ounced. However, slight wrinkles could be seen, particularly ound the nails nearest the edge of the gutter, which indicated that e cleats were overstressed.

Similar tests were also made on wide cleats such as shown in igure 18. No displacement or distortion of these cleats could be tected at any time during the tests.

It seems reasonable to infer, therefore, on the basis of these results at the wider cleats will give better service on seams with open cks, such as the ribbed, standing, and open double and single lock ams.

VII. SUMMARY

The following conclusions are based on the results of tests of seams r copper roofing:

1. Flat-lock seams calked with white lead and linseed oil can be sed wherever the depth of water which may be standing for several ys on the roof will not exceed 4 inches. Such conditions are rarely countered on copper roofs. The tests indicate that many years of rvice will not impair the weather-proof qualities of these seams. A ixture of white lead with 8 per cent of linseed oil is superior to one ith 15 per cent of oil.

2. Soldered seams were equally strong whether made with resin, id, or a "prepared" commercial flux. The least corrosive flux hould give the best results in the long run, since all appear to be qually satisfactory as regards strength.

3. Soldered seams made parallel or transverse to the direction of olling of the copper were equally strong.

4. The strength of soldered lap seams, one-quarter to 1 inch in idth, is proportional to their widths. The tensile tests showed that ap seams under three-quarter inch in width are not adequate for opper roofing. The proper width can not be determined from the sual tensile test, since it is necessary to take time under load into ccount.

5. A large increase in the amount of solder used on one-half-in flat-lock seams results in only a small increase in strength.

6. Pretinning by dipping the edges of the sheets to be joined molten solder or tin increases the strength of lap and flat-lock seam The increase is very marked in the case of flat-lock seams since this method it is possible to join all the layers of copper in the seam

7. The maximum safe load for soldered lap seams is approximately 350 lbs./in.^{2} (length times width) of seam, and for one-h inch pretinned flat lock seams 375 lbs./in.^{2} of seam. Under great loads failure will occur after a time, depending upon the magnitu of the load.

8. Cleats 2 inches wide are preferable to those only 1 inch wide.

WASHINGTON, May 7, 1930.

RP217

PARATUS FOR THE MEASUREMENT OF HIGH CONSTANT OR RIPPLED VOLTAGES [1]

By Lauriston S. Taylor

ABSTRACT

n improved form of high resistance to be used as a high-voltage voltmeter tiplier for use up to 150 kv. is described. The total resistance is 100 ohms, designed to be coronaless by placing one hundred 1-megohm resistors 0 corona cases containing 5 resistors each, the corona cases being mounted eries on top of each other. The complete unit is readily portable. Methods alibrating the resistance under full-load conditions are described. Errors discussed and necessary corrections, to give a maximum error in high-voltage surement of 0.01 per cent, are given. A new type of high-voltage string rometer for use in connection with the resistance is also described.

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I. INTRODUCTION

With the increasing use of high rippled or constant voltages for cise physical and commercial purposes, it is becoming more necesy to make accurate measurements of the magnitudes dealt with. these, the most difficult is the measurement of potential, yet in field of pure and applied X rays this is particularly important various reasons.

ince the early work of Farnsworth and Fortescue,[2] Chubb,[3] and k,[4] a. c. voltages have been measured largely with the sphere-rk gap for which an empirical calibration was established. This bration being independent of the frequency over wide ranges has ified its use to measure either rippled or constant voltages. How-r, to attain the highest accuracy by such a means the spheres st be so large (25 to 50 cm diameter) that it almost eliminates their

[1] to the present the term "constant potential" has been used indiscriminately in describing the tial supplied by kenotron or other valve tube rectification. Accordingly we will in the future use a more accurate designation of voltages which are actually not constant but fluctuate about a certain ge value. We thus define a "Ripple Quantity" (potential or current) as a simple periodic quantity $+V_1 \sin(\omega x+\alpha_1)+V_2 \sin(2\omega x+\alpha_2)+\ldots$ in which the constant term (V_a) is so large that all values quantity are positive (or negative). The amount of ripple ("Ripplage" or "Ripplance") in a ripple ity is the ratio of the difference between the maximum and minimum values of the quantity to the ge value.

e above definitions are being considered by the Committee on Electrical Definitions of the American ards Association under the sponsorship of the A. I. E. E.

[2] W. Farnsworth and C. Fortescue, Trans. A. I. E. E., **32**, pt. 1, p. 733; 1913.

[3] W. Chubb and C. Fortescue, Trans. A. I. E. E., **32**, pt. 1, p. 739; 1913.

[4] W. Peek, G. E. Rev., **16**, p. 286; 1913; and Trans. A. I. E. E., **32**, pt. 1, p. 812; 1913.

use in the ordinary laboratory. In addition, the construction details must conform to certain arbitrary specifications, and corrections must be made for atmospheric conditions. With the 125 mm spheres more commonly used, the errors increase until the precision necessary for many physical purposes is no longer obtainable.

Another important disadvantage of the sphere-gap method is that its use necessarily interrupts the high voltage which it is to measure. This is particularly troublesome in the case of the usual ripple voltage obtained from kenotron-condenser rectifier circuits.

Various types of electrostatic voltmeters have been devised for measuring these high voltages. They have been calibrated in most cases either with a 125 mm sphere gap or by means of the short wave-length limit of the X-ray continuous spectrum using the relation $V = 1.234/\lambda_o$ where V is the maximum voltage expressed in kilovolts and λ_o is the spectrum limit expressed in angstroms. The sphere-gap method of calibration is limited by the inaccuracies of the sphere gap used; the second is possible only in a well-equipped X-ray laboratory having an accurate ionization X-ray spectrometer. A high precision absolute electrometer for a. c. potentials up to 250 kv. has been built by Brooks,[5, 6] but unfortunately is not applicable to d. c. voltage measurements.

Thus far, the only accurate method of measuring high d. c. potentials has been by means of a high resistance used as a voltmeter multiplier. This method has been employed by Webster, Duane, and Terrell; and, while serving well the particular purpose, the resistances have been unwieldy and have drawn considerable power from the high-voltage source.[7]

As a part of the bureau's program of practical X-ray studies it was considered necessary to make a careful study of high voltages under actual operating conditions. This has necessitated the construction and calibration of accurate electrostatic voltmeters and small sphere gaps. For this there has been developed a compact and portable voltmeter multiplier which consumes but 1 milliampere at 100 kv. and hence can be maintained in continuous connection with the usual high-tension system without interfering with its operation.

II. CONSTRUCTION AND TEST OF MULTIPLIER RESISTORS

1. CONSTRUCTION OF INDIVIDUAL UNITS

It was desired to make the unit of standard materials, if possible; hence, a number of different types of commercial resistors were tried. Those finally selected were 1-megohm units of nickel chromium wire with a special insulation designed to withstand both high temperatures and high voltage. Nickel chromium was chosen in spite of its comparatively large temperature coefficient because manganin or constantan would have made the units too bulky. In these resistors the wire is wound on six-spool bobbins, 1 megohm to each, as shown in Figure 1.

[5] See L. S. Taylor, B. S. Jour. Research, **5** (RP211), p. 507, October, 1930.
[6] See C. Snow, B. S. Jour. Research, **1** (RP17), p. 513; 1928.
[7] H. M. Terrell, C. T. Ulrey, X-Ray Technology, pp. 112-116, Van Nostrand; 1930.
[8] L. S. Taylor, B. S. Jour. Research, **2** (RP56), p. 771; 1929.
[9] L. S. Taylor, B. S. Jour. Research, **3** (RP119), p. 807; 1929.

Two kinds of bobbin material, both of which proved satisfactory, were used: (*a*) Lavite, carefully baked after machining and then impregnated with paraffin; and (*b*) isolantite, which is supposedly less likely to absorb moisture. The spools are wound successively and the bobbins practically noninductively by reversing the direction of winding in adjacent spools, the wire passing from one spool to the next through the slot in the partition,[10] and its ends soldered to brass studs cemented into the ends of the insulating base. X-ray photographs were made of several to inspect the effectiveness of the cement and to reveal possible leakage paths through the insulation.

2. TEST OF INDIVIDUAL UNITS

The manufacturer's rating for each unit was given as 1 megohm ±1 per cent with an energy dissipation of 1 watt. With each unit subjected in air to an applied potential of 1,000 volts, d. c., for 8 hours no indication of breakdown appeared. With 1,415 volts, d. c. (2 watts), for 2 hours, the result indicated that a 100 per cent overload was safe; 2,000 volts (4 watts) for 2 hours caused breakdown in only 3 per cent of the units tried. These tests, repeated with the units immersed in ordinary high-tension transformer oil, showed no breakdowns.

A special high-voltage Wheatstone bridge was constructed so that the resistance of the bobbins could be measured under load conditions. In the two arms of the bridge on one side of the galvanometer were placed, respectively, the unknown resistor of about 1 megohm and a dial manganin resistance box, ranging from 0 to 1,111,111 ohms in 1-ohm steps. In the other two arms were placed manganin resistances of 5,000 ohms each. Voltages up to 2,000 volts, d. c., were applied directly to the bridge. With this operated at 1,000 volts it was possible to detect a change in resistance of the bobbins of 1 part in 100,000, although the absolute accuracy was limited to 0.01 per cent by the uncertainty in the calibration of the bridge arms.

With this bridge it was readily possible to examine any unit under operating conditions and detect any failure of the resistor, such as a breakdown between windings at high voltage. To determine the temperature coefficient of resistance, the resistor was immersed in a large beaker of transformer oil heated to 80° C., and resistance measurements made with the bridge every few minutes as the oil (well stirred) cooled down to room temperature. The results, plotted in Figure 2, gave a temperature coefficient of 0.0152 per cent per ° C. All resistance measurement at other room temperatures were corrected by this coefficient to 20° as standard.

For determining the resistance of each bobbin, two methods were used: (*a*) With low voltage (25 volts) applied to the bridge continuously, and (*b*) with high voltage (1,500 volts) applied for about one second, followed by a long interval of rest during which the bridge was adjusted in preparation for the next trial for balance. In neither case was appreciable heating of the coil produced. Results by the two methods agreed to better than 0.1 per cent, and thus justified the use of method (*a*) for routine measurements of room temperature resistance. Surface or body leakage of the lavite and

[10] Measurements made elsewhere have shown the inductance to be slightly negative but negligible for the purpose at hand.

isolantite was tested by connecting an unwound bobbin in ser with a galvanometer of sensitivity 10^{-8} amps per millimeter and source of potential of about 1,300 volts, d. c. No measurable c rent passed through, indicating the resistance to be greater than 1 ohms and negligible as a source of leakage. A leakage test with t hard-rubber supports, similar to that for the bobbins, proved th insulation to be satisfactory also.

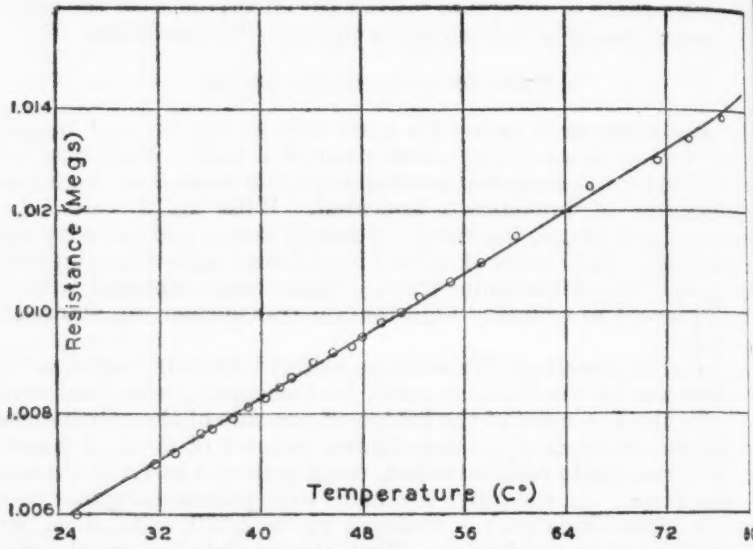

FIGURE 2.—*Curve for obtaining temperature coefficient of a single resistor*

III. CONSTRUCTION OF THE COMPLETE UNIT

For the purpose at hand a resistance suitable for the measuremen of 150 kv. was needed. As a result of the above tests, 100 megohms were shown to carry 150 kv. safely, thereby giving a working current of 1.5 milliamperes and dissipating a maximum of but 225 watts. Connecting 100 resistors in series in open air would have resulted in excessive corona around those at the higher potentials and thus introduced three serious difficulties: (*a*) Corona bombardment which would eventually break down the insulation of the wire, (*b*) the precipitation of dust from the air which would eventually cause serious surface leakage, and (*c*) the possibility of a corona current of sufficient magnitude to introduce error. This might be avoided by immersing 20 bobbins in series in a 1½-inch pyrex tube filled with high-tension transformer oil. By so doing the maximum potential difference between the ends of the tube would be only 30 kv., thus eliminating excessive circulation of the oil. Five such units in series, properly suspended in air and kept free from dirt, would provide a fairly suitable multiplier for 150 kv. This method is open, however, to two main objections: (*a*) It is difficult to get at the individual resistors to measure their resistance, and (*b*) the oil may eventually break down sufficiently to cause appreciable leakage.

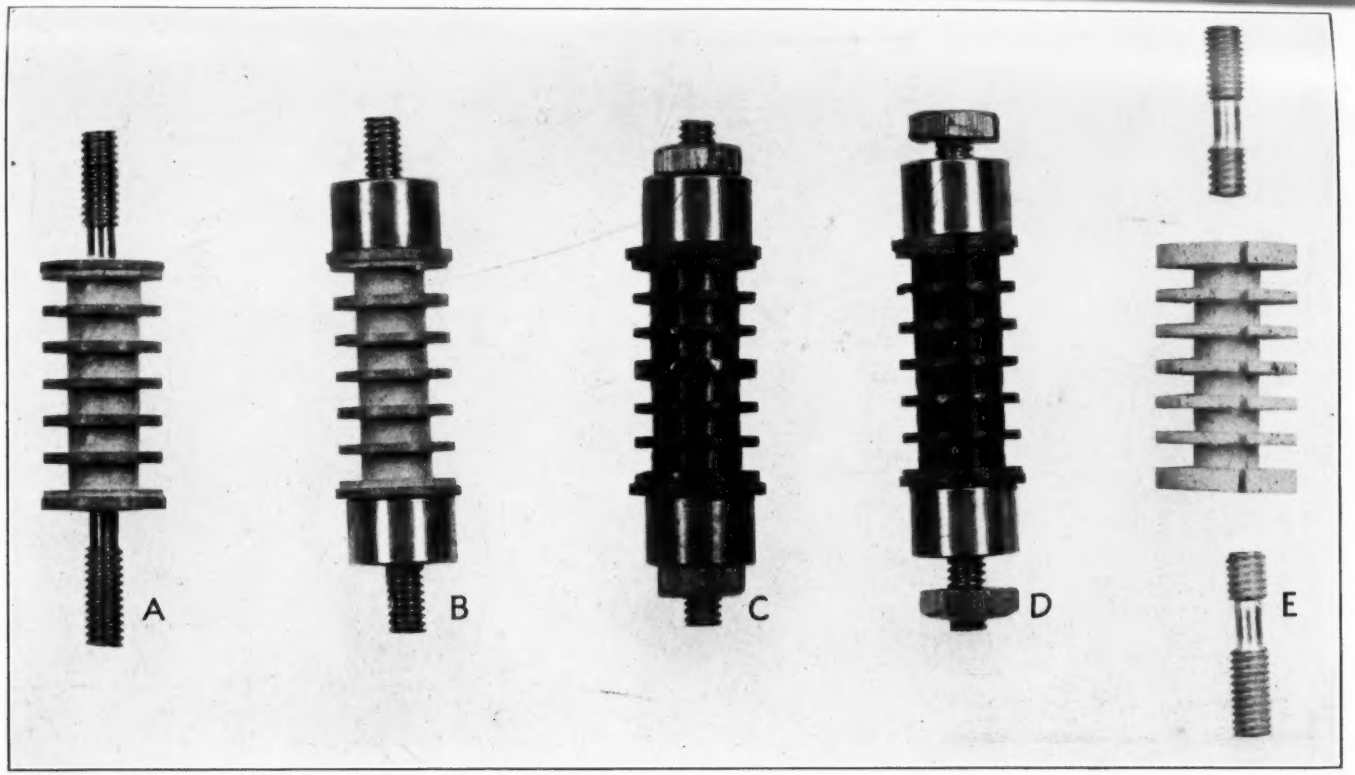

FIGURE 1.—*Wire resistors used in multiplier*

A, B, Lavite bobbins; *C, D,* complete resistor wound in 6 spools; *E,* Isolantite bobbin.

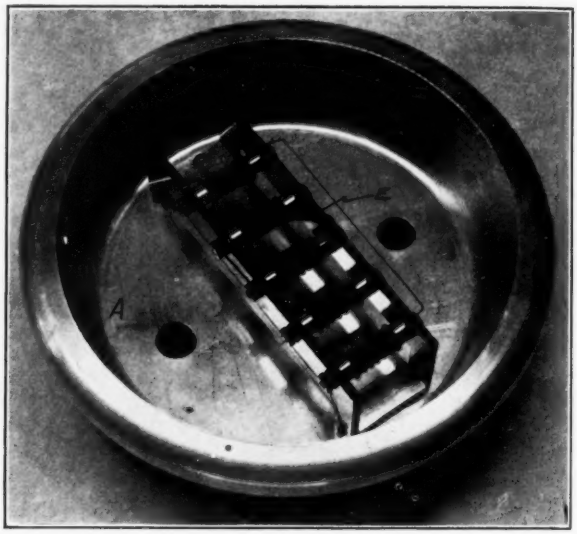

FIGURE 3.—*Assembled unit of five resistors in spun aluminum corona shield with cover removed*

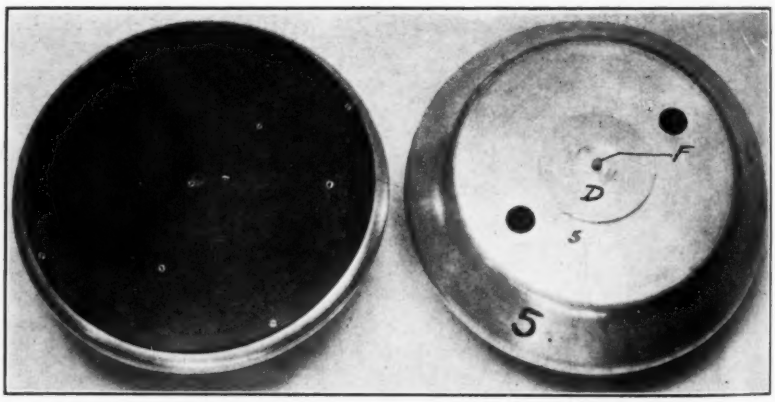

FIGURE 4.—*Complete unit with cover attached*

To eliminate the difficulties above, the 100 units were finally assembled into 20 sets of 5, each 5 being mounted in a spun aluminum corona shield, *A* (fig. 3), on a frame of polished hard rubber, *B*, carried by an aluminum base plate, *C*, which is bolted to the shield with a 3-inch disk of one-eighth-inch aluminum, *D*, serving as a nut. The resistors are connected in series in such a way that only 40 per cent of the potential applied to a shield exists between each bobbin and its nearest neighbor and thus effects a minimum potential difference along the hard rubber support.

One end of this group resistance is permanently fastened to the shield, and the other end to a flat phosphor bronze spring, *E*, mounted on the hard rubber frame. Covering the open face of the corona shield is a one-fourth-inch hard rubber disk. (Fig. 4.) In both shield and cover are two 1-inch holes to provide ventilation. A stud, *F*, protruding from the aluminum disk, *D*, is screwed into the hard rubber cover of the next corona case so as to make electrical contact with the spring *E*.

For convenience, 2 stacks of 10 shields each were supported (fig. 5), top and bottom on electrose insulators mounted in a dried oak frame which had been painted with several coats of shellac. These frames can be used separately as in Figure 5 or placed one on top of the other and connected in series as in Figure 6.

The assembled multiplier has the following advantages: (*a*) The maximum potential difference between any resistor and its surroundings is only 7.5 kv.; hence, there will be no corona inside the shield and a minimum of dust precipitation; (*b*) all corona shields are maintained at a fixed potential difference of 7.5 kv., maximum, with respect to adjacent shields, so the total stack is coronaless; (*c*) the electrostatic shielding effect of the corona case protects the hard rubber cover of the next above from corona bombardment; (*d*) the small gap between corona case minimizes the possibility of sunlight affecting the insulating qualities of the hard rubber; (*e*) dull black lacquer on the inside and outside of the corona cases permits a maximum of heat radiation;[11] (*f*) the separation into 5 megohm units permits easy tests for possibly defective resistors, and likewise a ready calibration of the resistance of each.

It might be pointed out that for continuous use, the hard rubber deforms appreciably. This has been avoided by making the covers of one-fourth-inch pyrex glass plates, pyrex being used in preference to other glass because its surface leakage is small. The stack is, however, rendered more fragile. For measurements of short duration, hard rubber has proved to be satisfactory, and, moreover, furnishes a readily portable apparatus.

IV. PERFORMANCE TESTS

It was found that the assembled stacks, when subjected for several hours to high d. c. potentials up to 75 kv. (per stack), carried the load without damage. The resistance of each case was measured before and after application of the voltage, as described above, with approximately one-fifth of the maximum working voltage applied

[11] The size of the corona case is such that 10 resistors might have been placed in each instead of 5. However, this is undesirable, since it would double the amount of heat to be dissipated per unit and cause additional heating of the coils.

across the case. The few units which showed any change in resistance were then discarded.

It was impossible in actual operation to make any measurement of the temperature attained after temperature equilibrium had been reached, since this is affected by the proximity of other heated coils and the restricted air space of the corona case. However, a temperature correction for single resistors may be determined as a function of the current passing through the coil. This is obtained by applying a given potential to the single resistor and measuring the resistance after equilibrium has been reached. A curve may then be plotted giving directly the change in resistance as a function of either the voltage drop or the current in the coil. A number of resistors were so tested in open air and the characteristics of all were found to be exactly the same.

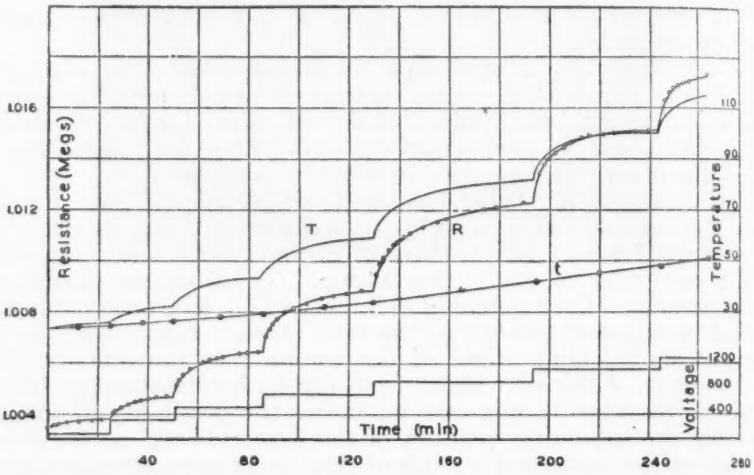

FIGURE 7.—*Resistance curves to show effect of heating of the resistors under operating conditions*

Voltage increased by steps.

To determine the correction for an assembled stack, one resistor in the center was detached from the main circuit and leads taken out to the Wheatstone bridge by which the resistance was measured at room temperature and corrected to 20° C. Next the resistance was measured for a series of potentials up to the maximum while in each case a potential from an independent source of 49 times the bridge potential was applied to the remaining 49 units in series. By this means the resistance of a single unit under actual operating conditions of voltage and heat radiation was obtained, the measurements being made at a given potential every two or three minutes until equilibrium was reached.

The results of this are plotted in Figure 7 for potentials up to 1,300 volts per resistor. Examination of the curves shows that equilibrium, within about 0.02 to 0.03 per cent, is reached in about 20 minutes. Having the no-voltage resistance at 20° C., the percentage correction for each voltage (or corresponding current) was calculated from these curves.

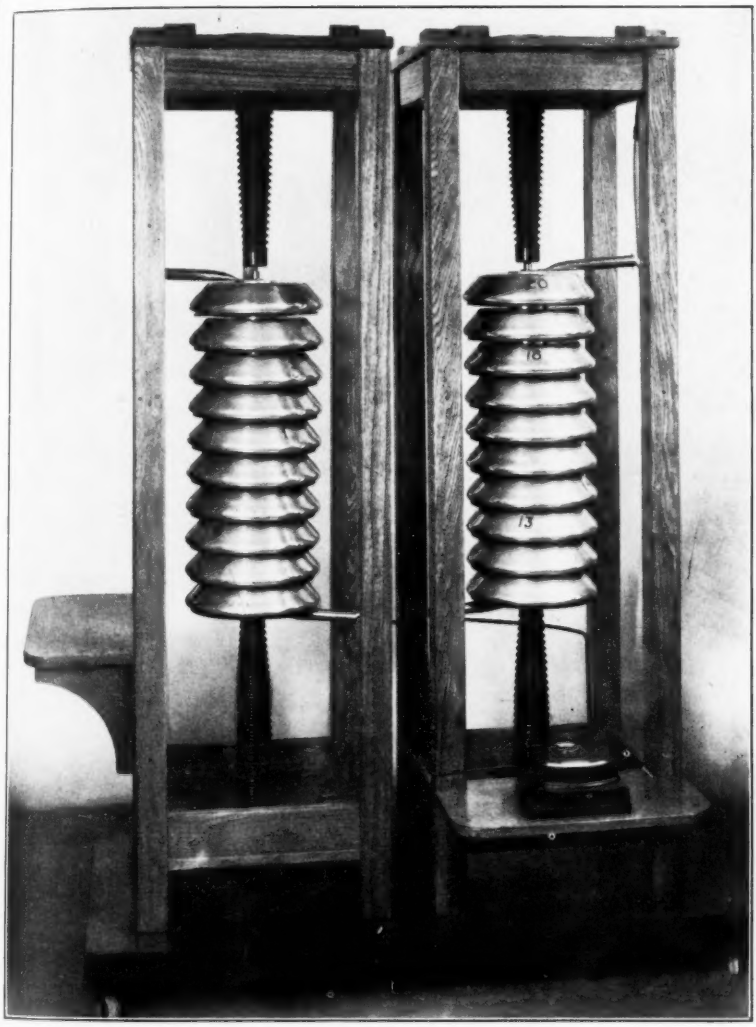

FIGURE 5.—*Assembled resistor of 50 megohms per stack*

In the particular case shown a microammeter is in a grounded circuit dividing the stacks.

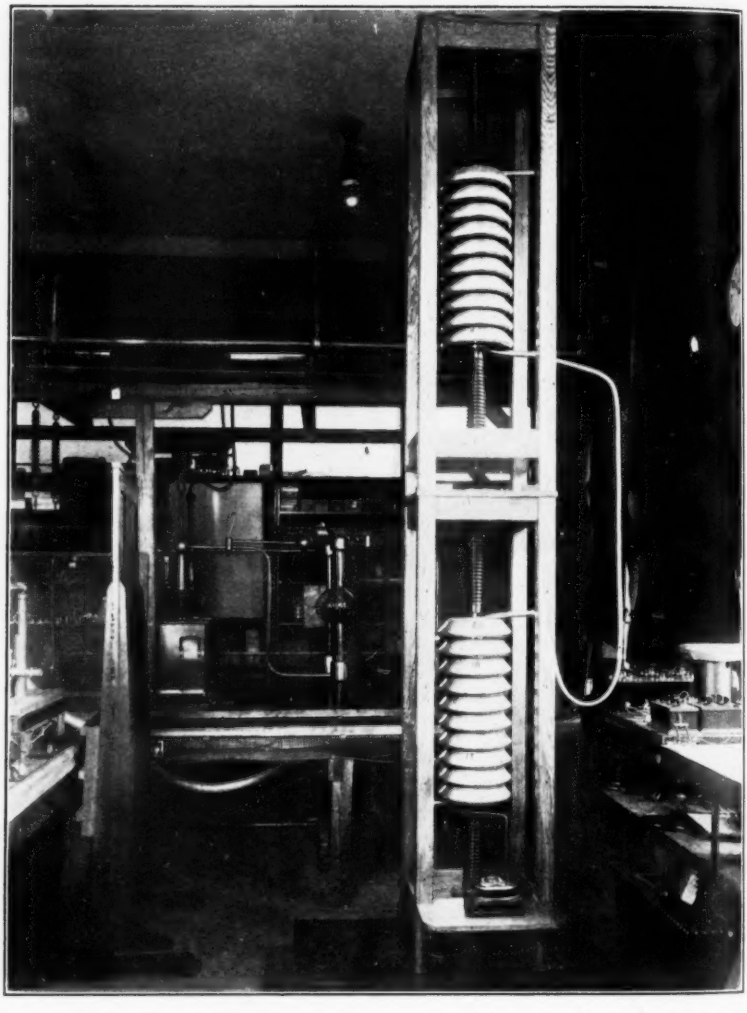

FIGURE 6.—*Two 50-megohm stacks, connected in series and mounted one above the other*

At right can be seen the high-voltage bridge and in the background a part of the high-voltage generator.

Curve *a* Figure 8 shows the correction to be applied to the resistance when the reading is taken 20 minutes after the potential is applied. Thus, when using the stack for voltage measurements, this curve gives for every current the necessary correction for the resistance to within 0.02 per cent. Curve *d* shows a similar result for 40 minutes readings. Curves *b* and *c* give corrections for readings taken, respectively, 10 and 5 minutes after application of voltage. The fact that *b* and *c* are smooth curves indicates that such readings are just as reliable as those taken nearer equilibrium. The difference between any two of these correction curves is only about 0.04 per cent so that great care does not need to be taken in timing the duration of the current. When neglecting corrections, the error is only of the order of 1 per cent.

Curve *T* in Figure 7 shows temperature of the coils as calculated from their temperature coefficient, while curve *t* gives the air temperature within the corona case, indicated by a mercury thermometer inserted through one of the holes.

The same correction was found when voltages were brought up to the desired value instantly instead of in steps.

It should be mentioned that a correction must be made, of course, for any room temperature differing from that at which the resistance was calibrated under no-load conditions. In the present case the no-load resistance must be increased by 0.015 per cent for each degree rise in temperature of the room above 20° C.

V. APPLICATION TO HIGH D. C. VOLTAGE MEASUREMENTS

The application of such a resistance to high-voltage d. c. measurements is well known and straightforward, and consequently need not be dealt with in detail.[12] Two methods are common: (*a*) To measure the potential drop v across a small known resistance r in series with the high resistance R, calibrating the galvanometer with a standard cell for each reading; and (*b*) to make a direct measurement, by means of a suitable galvanometer or microammeter, of the current i flowing through the resistance. By method (*a*) the high voltage V_o is given by $V_o = v(R+r)/r$ where R is the total resistance. By method (*b*) the voltage is given by Ohm's law, $V_o = iR$.

For some purposes; for example, our X-ray studies, it may be desired to make not only an accurate measurement of the high potentials, but to determine also the magnitude of any small irregular fluctuations in the ripple voltage. To do this a new type of high-voltage electrometer was developed suitable for measuring voltages up to 1,000 volts to within ±0.1 per cent. (Figs. 9 and 10.) A drawn platinum wire, *A*, of 0.01 mm diameter (shown in a heavy line) is suspended about 2 mm from a 2.5 cm brass tube, *B*. This wire is under the tension of a loop of coarse quartz filament *C* at the lower end and its adjustable suspension above. This system is surrounded by a cylindrical copper case about 5 inches in diameter, supported at the base by a good insulator. With the case grounded and a potential applied to the inner insulated system, consisting of tube and wire, we have an idiostatic electrometer the sensitivity of which may be altered at will by changing the tension on the wire.

[12] See footnote 7, p. 610.

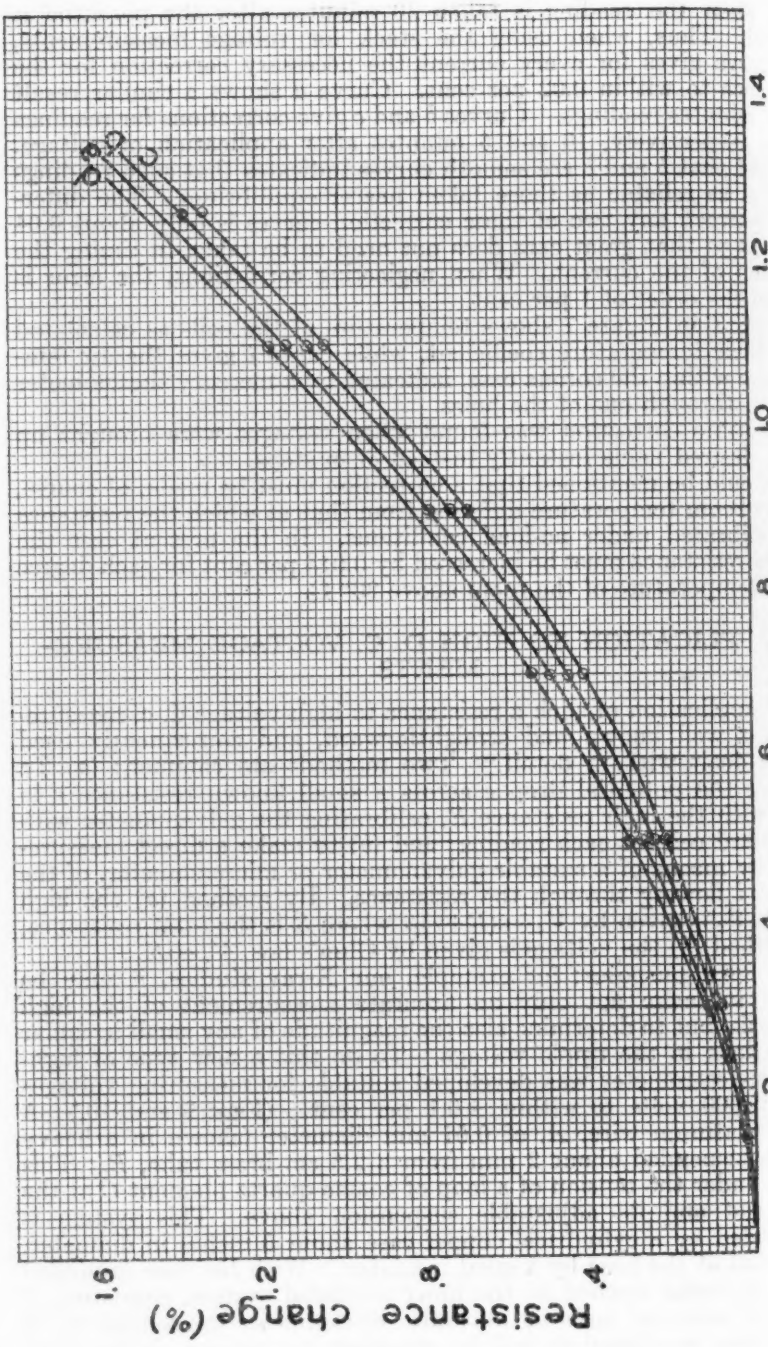

FIGURE 8.—*Curves showing the percentage correction to be added to the total resistance to correct for heating*

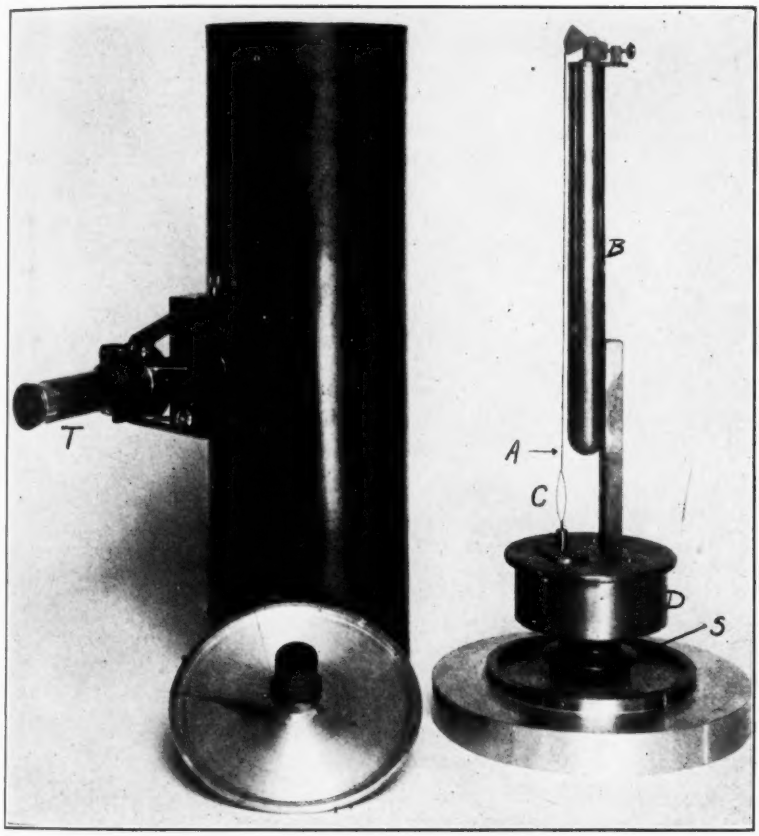

FIGURE 9.—*Details of electrometer*

Fiber and quartz loop have been drawn in so as to be visible.

The period of the wire is so short that it follows rapid fluctuations in voltage.

The displacement of the fiber is observed by means of the telescope, *T*, provided with an ocular scale of 100 divisions. By suitably adjusting the fiber tension the electrometer will deflect 100

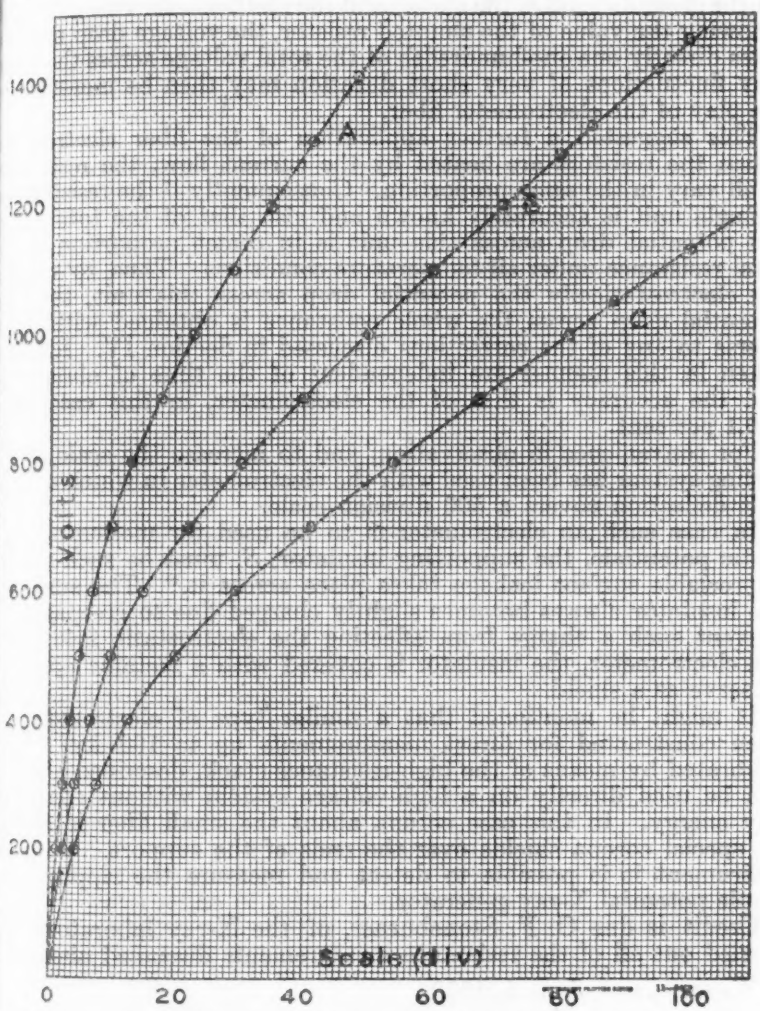

FIGURE 10.—*Calibration curves for high-voltage idiostatic electrometer*

Fiber tension for curve *B* less than for curve *A*, etc.

divisions per 1,000 volts, and readings can be readily made to within one-tenth division, which is equivalent to about 0.2 volt at the extreme end of the scale. Calibration of the electrometer is effected by means of a 1,500-volt d. c. generator. As an alternative, the zero may be set off scale and the fiber tension adjusted to bring the desired voltage range on the scale.

Figure 10 shows three calibration curves for the electrometer when the tension, t, of the fiber is changed ($t_A > t_B > t_C$). Thus, in measuring a potential of the order of 1,000 volts, the conditions represented by curve C are most suitable. In using this instrument, as suggested above, it is shunted around the last 1 megohm resistor (at the grounded end of the stack) and the electrometer case grounded. Knowing the value of the shunted resistor, the voltage drop across it gives directly one one-hundredth of the total voltage across the stack. Any fluctuations of very short duration may then be measured by the play of the electrometer fiber.

This suggested a further application of the fiber electrometer. When the resistors are heated by the current flow, the resistances of all vary in the same proportion. Consequently if the resistance of a single unit is accurately known and also that of the total stack, the potential drop across this unit is in direct proportion to the total resistance under all temperature conditions. Thus, by measuring electrostatically the potential drop across this unit, the total potential drop across the whole resistance is obtained without recourse to any of the corrections discussed in Section IV. Readings taken in this manner are independent of the time of observation and the accuracy is that of the electrometer, in this case about ± 0.1 per cent.

For convenience in observation, and to increase the scale, a projecting system has been used with the electrometer in which a 1,000-volt deflection covers a 500 division scale.

In case such an electrometer is to be used for measuring high-static potentials, the supporting insulator, S, must be such that no appreciable surface leakage takes place across it.[13] The surface of the insulator always becomes slightly charged due to creepage. To prevent such a charge from affecting the electrostatic field within the electrometer, the insulator is covered with a metallic apron, D, to serve as a shield.

It might be mentioned that a similar type of electrometer has been constructed for direct measurements up to 100 kv. When calibrated by means of the high-resistance stack, described above, it can be used directly on a high-voltage system without consuming any energy. In this case corona about the small fiber is avoided by special corona shields over the ends of the support. With this instrument it is possible to detect and measure the ripplage of a ripple potential X-ray generator.

Credit is due C. F. Stoneburner, of the X-ray laboratory, who carried out all of the resistance measurements discussed above.

WASHINGTON, June 4, 1930.

[13] Bakelite is unsuitable for such insulation.

COMPRESSIVE TESTS OF BASES FOR SUBWAY COLUMNS

By James H. Edwards, H. L. Whittemore, and A. H. Stang

ABSTRACT

In the construction of subways under the streets for carrying passengers by electric trains it is customary to provide steel columns between the tracks to support the overhead structure. These columns are usually rolled steel H-sections having plate and angle bases riveted to the columns for distributing the load on the concrete footing.

Tests were made of 3 welded bases and 6 riveted bases, 3 without base plates, and 3 with base plates to determine whether the welded design was satisfactory. The specimens were loaded with the base on a span of 12 inches.

Some hand strain-gage readings were taken to study the stress distribution.

The strength of the welded specimens and the riveted specimens having base plates was practically the same. The H-section deformed greatly at the maximum load, and the stiffeners in the base buckled.

The strength of the riveted specimens without base plates was about 60 per cent of the strength of the other types. At failure, eight rivets on one side of the specimen sheared. There was apparently no deformation of either the H-section or the angles forming the base.

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I. THE COLUMN BASES

In the construction of subways under the streets for carrying passengers by electric trains it is customary to provide steel columns between the tracks to support the overhead structure. These columns are usually rolled steel H-sections having plate and angle bases riveted to the column for distributing the load on the concrete footing.

The American Bridge Co. suggested to the Interborough Rapid Transit Co., of New York City, that the bases be welded instead of riveted and that the design of the base be changed to one which was more suitable for this new method of fabrication. The welded base consisted of only three plates, as shown in Figures 1, 5, and 8. Six angles and two plates were required for the riveted base having no base plate, as shown in Figures 1 and 8, six angles and three plates for the riveted base having a base plate, as shown in Figures 1, 2, 3, 7, and 8.

As the welded design was a radical departure from the method of fabricating these important connections, which experience had shown to be satisfactory, tests were made to determine the strength of welded bases and 6 riveted bases, 3 without base plates and 3 with base plates. Some hand strain-gage readings were taken to study the stress distribution.

The American Bridge Co. made the designs and fabricated the specimens. The tests were made by the National Bureau of Standards.

II. METHOD OF TESTING

1. LOADING THE SPECIMENS

The specimens rested on two blocks, *A*–*A*, having cylindrical lower surfaces as shown in Figure 2. The blocks rested on a hardened steel plate, *B*. The blocks were 6 inches wide and 10 inches long. The radius of the cylindrical surface was 4 inches. The distance between the inner surfaces of the blocks, 6 inches, was about the nominal depth (5.986 inches) of the H-section. The span was therefore, 12 inches. A hardened steel plate, *C*, was placed on top of the H-section and the load applied through a spherical bearing, *D*.

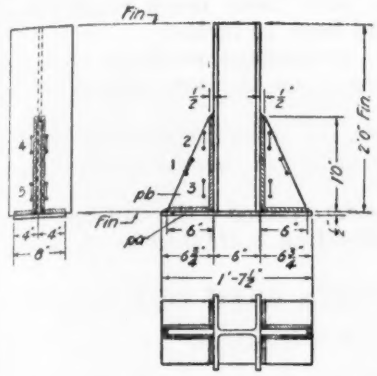
With an assumed yield point of 35,000 lbs./in.,[2] the H-section (sectional area 14.70 square inches) would be expected to fail in compression under a load of about 500,000 pounds. The testing machine having a capacity of 600,000 pounds was therefore used for these tests. The riveted bases without base plates failed when loaded in this machine, but as the other specimens did not fail under a load of 600,000 pounds, greater loads were later applied in the hydraulic testing machine having a capacity of 10,000,000 pounds. (See fig. 3.) Since the lower platen of this machine has a spherical seat, no spherical bearing was used on top of the H-section.

2. STRAIN GAGE MEASUREMENTS

To determine the stresses in some portions of the specimens, hand strain-gage readings were taken on the gage lines (shown in fig. 1) with a Whittemore fulcrum-plate strain gage having a 2-inch gage length. This strain gage (shown in fig. 4) was designed by one of the authors at the request of the Engineering Foundation, Committee on Arch Dam Investigation.[1] For that investigation a more accurate strain gage was desired than the instruments then available.

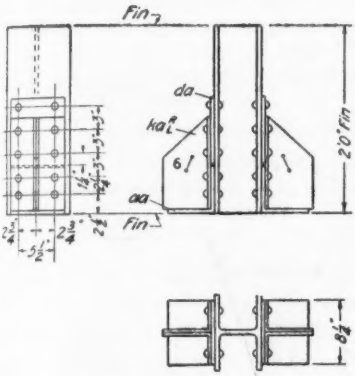
The frame of this instrument consists of two parallel side bars connected near their ends by spring fulcrum plates which effectively prevent motion of one bar relative to the other, except longitudinally. The two points (for insertion in holes in the member upon which the measurements are to be taken) are rigidly attached, one to each side bar. The relative movement of the side bars is, for an instrument having a 2-inch gage length, usually indicated by a "Last Word" dial micrometer graduated to 1/10,000 inch and having a range of 0.024 inch. Although the accuracy of the readings of this strain gage depends somewhat upon the skill of the observer, the error in the stress computed from the readings taken with this instrument having a 2-inch gage length, probably, did not exceed

[1] Engineering Foundation Committee on Arch Dam Investigation, Report by Committee, I, published by Am. Soc. of Civil Engrs., Strain-Gage, p. 64; May, 1928.



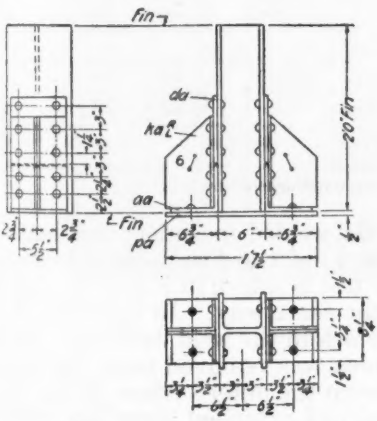
Welded

Bill of Material				
No. Pcs.	Shape	Length Ft.	Length In.	Remarks
1	6"H-CB61-50 lb. per ft.	2	0	Fin
1	Plate-8"×½"	1	7½	pa
2	Plates-6"×¾"	1	0	pb



Riveted, No Base Plate

Bill of Material				
No. Pcs.	Shape	Length Ft.	Length In.	Remarks
1	6"H-CB61-50 lb. per ft.	2	0	Fin
2	Angles-6"×6"×⅞"	0	8¼	aa
4	Angles-8"×4"×⅜"	0	11⅜	ka Fin
2	Plates-8"×⅞"	0	8½	da



Riveted, Base Plate

Bill of Material				
No. Pcs.	Shape	Length Ft.	Length In.	Remarks
1	6"H-CB61-50 lb. per ft.	2	0	Fin
2	Angles-6"×6"×⅞"	0	8¼	aa
4	Angles-6"×4"×⅜"	0	11⅜	ka Fin
2	Plates-8"×⅞"	0	8½	da
1	Plate-8"×½"	1	7½	pa

FIGURE 1.—*Dimensioned drawing of bases for subway columns*

2,000 lbs./in.^{2} The error would have been much smaller (abou 500 lbs./in.^{2}) if the gage length had been 10 inches.

On the riveted column bases, strain-gage readings were take only on the four inclined gage lines, *6*, on the outstanding leg of th stiffener angles.

Twenty gage lines were used on the welded specimens as shown in Figure 1 to obtain a better knowledge of the stress distribution i this new design.

To allow the average stress to be determined if the stiffener buckle the gage lines *1*, *2*, and *3* were placed on both sides of the stiffene

III. RESULTS OF THE TESTS WITH DISCUSSION

1. STRENGTH OF THE BASES

The results of the compressive tests are given in Table 1. I addition to the strength a "yield point" was obtained by observin either the load at which the beam of the testing machine "dropped" or the load which remained constant as the specimen shortened. A it was necessary to stop the testing machine to take the strain-gag readings, it was difficult to detect "yield points" by "drop of th beam" at loads near those at which strain-gage readings were taken

TABLE 1.—*Results of compressive tests of column bases*

[Nominal area of H-section, 14.70 square inches]

Column base No.	Description of specimens	Yield point		Strength	
		Total load	Stress in H-section	Total load	Stress in H-section
		Pounds	*Lbs./in.*^{2}	*Pounds*	*Lbs./in.*^{2}
TC 1–A	Welded	[1] 412,000	28,000	623,000	42,40
TC 1–B	do	444,000	30,200	666,000	45,30
TC 1–C	do	448,000	30,500	661,000	45,00
	Average				44,20
TC 2–A	Riveted, no base plate	395,000	26,900	419,000	28,50
TC 2–B	do	353,000	24,000	426,000	29,00
TC 2–C	do	367,000	25,000	416,000	28,30
	Average				28,60
TC 3–A	Riveted, base plate	435,000	29,600	698,000	47,50
TC 3–B	do	446,000	30,400	683,000	46,50
TC 3–C	do	440,000	29,900	676,000	46,00
	Average				46,60

[1] At this load no drop of the beam was observed, but the stiffeners were buckled.

The first indication of failure in the welded specimens was buckling of the stiffener plates. The H-section deformed as the load increased. The welded specimen TC 1–A after test is shown in Figure 5. All the welded specimens failed in much the same way. In only one of the welded specimens, TC 1–A, was a crack in the weld detected. It was not observed until after the specimen was removed from the testing machine. It was at A (fig. 5) between the outer surface of the flange of the H-section and the weld metal and extended along the weld for about three-fourths inch. It was probably caused by the increase in the angle between the base plate and the flange of the H-section

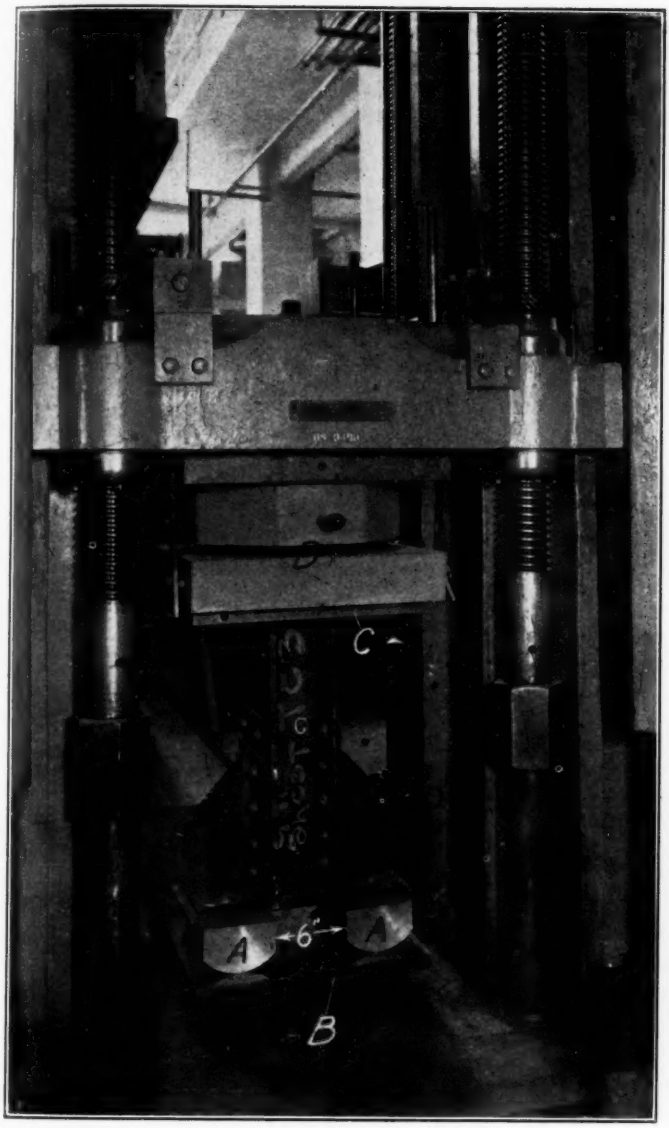


FIGURE 2.—*Specimen ready for test in the testing machine having a capacity of 600,000 pounds*

The base was supported on a span of 12 inches by blocks having cylindrical (radius 4 inches) lower surfaces. A spherical bearing block was placed on top of the specimen. This specimen is riveted base TC 3–C having a base plate.

FIGURE 3.—*A specimen after test in the testing machine having a capacity of 10,000,000 pounds*

This is the riveted base TC 3-A having a base plate. The total load was 698,000 pounds and the average stress in the H-section was 47,500 lbs./in.^{2}

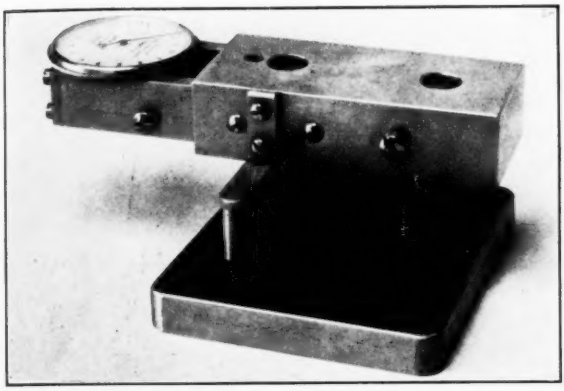


FIGURE 4.—*The Whittemore fulcrum plate strain gauge having a gauge length of 2 inches*

FIGURE 5.—*The welded base TC 1–A after test*

The total load was 623,000 pounds and the average stress in the H-section was 42,400 lbs./in.^{2} The crack shown at A was the only one detected in a weld for the three specimens of this type.

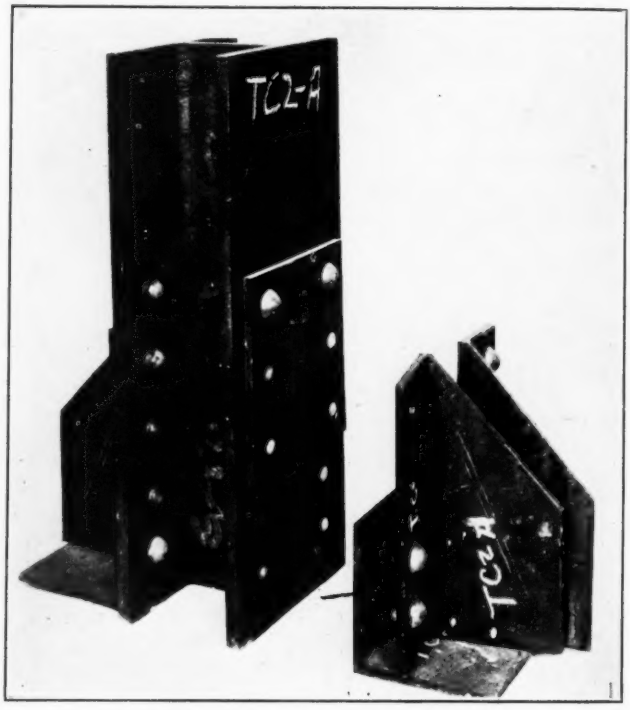


FIGURE 6.—*The riveted base TC 2–A without base plate, after test*

The eight rivets on one side of the specimen sheared. The total load was 418,000 pounds, and the average stress in the H-section was 28,480 lbs./in.^{2} The average shearing stress in the sixteen ¾-inch rivets was 59,400 lbs./in.^{2}

when the H-section deformed. The crack was so small that it could have had no effect on the results of the test.

All the riveted specimens without base plates failed by shearing the eight rivets on one side. Specimen TC 2–A after test is shown in Figure 6. There was no noticeable deformation of the H-section nor of the pieces forming the base.

The computed average maximum shearing stress in these rivets, using the nominal area of the 16 three-fourth-inch rivets, was 59,400 lbs./in.^{2}

The failure of the riveted specimens with base plates was similar to that of the welded specimens as may be seen in Figures 3 and 7. The outstanding legs of the stiffener angles buckled, several rivets sheared, and the H-section deformed.

The strength of these particular welded specimens was practically the same as the strength of these particular riveted specimens having base plates. The strength of the riveted specimens without base plates was 61 per cent of the strength of the riveted specimens having base plates. Unfortunately no tensile specimens of the steel in these column bases were provided by the fabricator. There is no record as to whether the H-sections were cut from the same or from different lengths. It is therefore impossible to draw general conclusions from the results of the tests. As there was considerable deformation of the H-sections for the welded and riveted base-plate specimens and comparatively little deformation of the base, it is probable that the maximum load was determined by the strength of the H-section.

As the maximum compressive strength of columns decreases as the length increases, the strength of the short H-sections used for these tests was greater than the strength of any longer column having the same section. It may also be pointed out that the bases, when in use, rest on flat surfaces supported by the foundation of the subway. Since these bases were tested on blocks which were spaced 12 inches center to center, they were, therefore, tested under more severe conditions than those which could occur in service.

2. STRESSES

The location of the gage lines on which strain gage readings were taken is shown in Figure 1. The stress along a gage line was computed[2] by multiplying the change in the length of the gage line by the assumed Young's modulus of elasticity of 29,000,000 lbs./in.^{2} for the steel. The readings for gage lines similarly located were averaged for specimens of the same type.

(a) STRESSES IN THE STIFFENERS

The stresses in gage No. 1 on the stiffener plates of the welded specimens, TC 1, may be compared with those in gage No. 6 on the stiffener angles of the riveted specimens TC 2 and TC 3. It should be remembered that the combined thickness of the two angles in the riveted specimens (three-fourth inch) is equal to the thickness of the stiffener plates in the welded specimen.

For convenience in plotting the graphs of Figure 8, the ordinates are the average stresses in the H-section computed from the load indi-

[2] For method of computing stress from strain-gage readings, refer to B. S. Tech. Paper No. 260, "Tests of Some Girder Hooks," by Whittemore and Stang, p. 310.

cated on the beam of the testing machine, while the abscissas are the stresses computed from the strain-gage readings. Each plotted point is the average of the six readings obtained for the two gage lines on opposite sides of the specimen for each of the three specimens. The stress in the stiffener plate (gage No. 1) is proportional to the average stress on the H-section up to about 18,000 lbs./in.^{2} and is more than twice the stress in the stiffener angles of the riveted specimens (gage No. 6). This shows that the riveted base is stiffer than the welded. The gage lines, Nos. 1 and 6, are in the same position relative to the base and the column. The greater stiffness of the riveted specimens is undoubtedly due to the fact that the stiffeners on the riveted bases had considerably more metal outside the gage lines than the stiffeners on the welded base. For higher loads the stresses in the stiffener plates increased much more rapidly than the average stress in the H-section, and eventually caused buckling.

The stress in the riveted specimens was proportional to the average stress in the H-section and was practically the same for the specimens with and without base plates.

Although base plates on the riveted specimens increased the maximum load about 60 per cent, they did not increase the stiffness of the base for loads below the yield point.

The stresses in the vertical gages Nos. 2 and 3 (fig. 1) on the stiffener plates of the welded specimens are plotted in Figure 8. The stress in gage No. 2, 9 inches above the base, was directly proportional to the average stress in the H-section throughout the loading range for which strain measurements were taken.

The stresses in gage No. 3, 3 inches above the base, were about the same as those in gage No. 2 up to about 8, 000 lbs./in.^{2} For higher loads, however, the stresses in gage No. 3 increased more rapidly than the stress in gage No. 2 and were much less than those in the inclined gage No. 1. It appears probable that the upward forces exerted on the specimen by the blocks, A–A (fig. 2), caused high compressive stresses in the stiffeners above the blocks. Although gage No. 3 was not vertically over the block, it was in the portion of the stiffener which was highly stressed.

(b) STRESSES IN THE H-SECTION

Strain gage readings on the H-section were obtained on only the welded specimens, TC 1. These gage lines (fig. 1) were vertical and centered 9 inches for gage No. 4 and 3 inches for gage No. 5 above the lower end of the H-section. The stresses on these gage lines have been plotted in Figure 8. The dashed line is inclined 45° to the axes and may, therefore, be called a line of theoretical stress since, if the load on the H-section was uniformly distributed over the cross-section, the strain-gage stresses would equal the average stress computed from the total load on the specimen. Because of the stiffeners and the base plate and the fact that the specimen was supported on a span of 12 inches, it is obvious that a uniform stress distribution should not be expected near the base of the H-section. Figure 8 shows that the stresses in gage No. 4, 9 inches from the bottom of the H-section, were less than the average stress in the H-section for low loads, but practically equal the average at 26,000 lbs./in.^{2} The stresses in this gage line were proportional to the

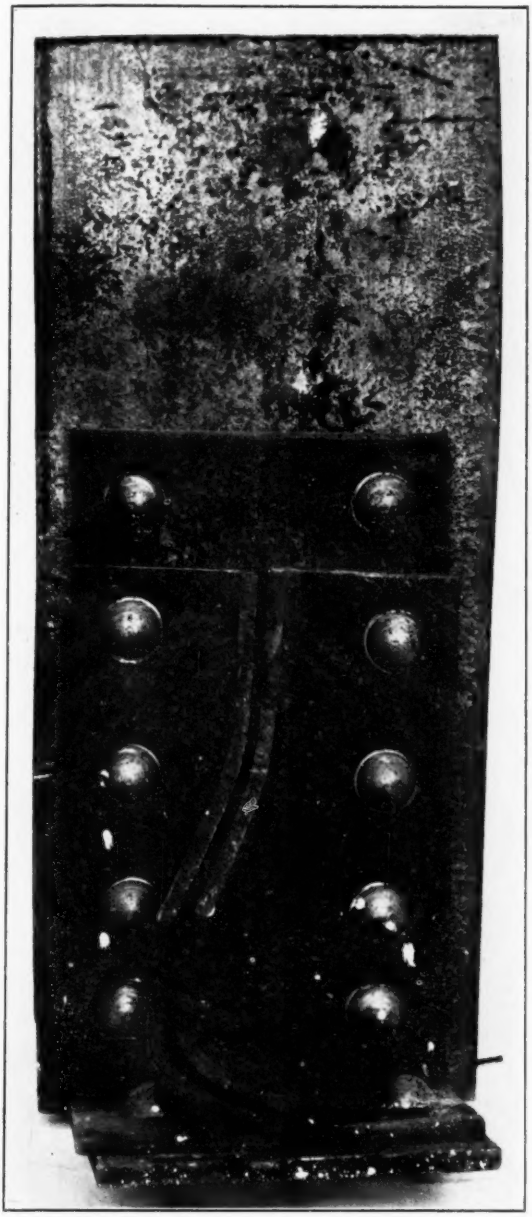


FIGURE 7.—*The riveted base TC 3–C having base plate, after test*

The total load was 676,000 pounds, and the average stress in the H-section was 46,000 lbs./in.²

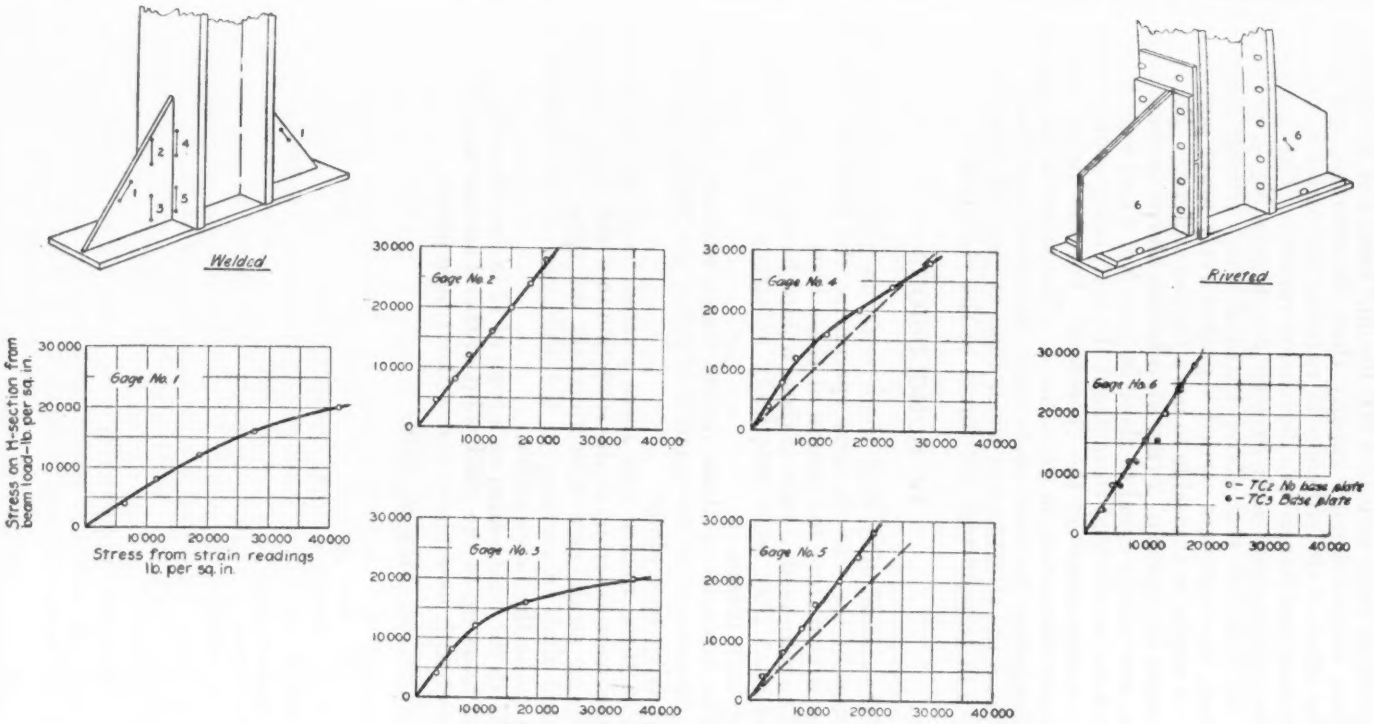


FIGURE 8.—*Stresses in the gage lines*

Gages 5 Nos. 1 to 5 were on the welded bases and gage No. 6 on the riveted bases

average stress from zero to 8,000 lbs./in.^{2} load, but for higher loads the stress increased more rapidly than the average, and indicated that the effect of the stiffeners in reducing the stress in this portion of the H-section flange was decreasing rapidly. The change in the direction of the stress curve for gage No. 1, gage No. 3, and gage No. 4 (fig. 8), indicates that above 12,000 lbs./in.^{2} average stress in the H-section, the stiffeners carried a progressively lower portion of the load. It might be advisable to use a thicker stiffener. For low loads the stresses in gage No. 5 (fig. 8), 3 inches above the base of the H-section, were about equal to those in gage No. 4 and were practically proportional to the load throughout the test, being about 70 per cent of the average stress in the H-section. For the higher loads, they were lower than those in gage No. 4. The stress in the web of the H-section, near the base plate must, therefore, have been low. At gage No. 5 the stiffener was wider than at gage No. 4 and was more effective in transmitting the forces to the H-section.

IV. CONCLUSIONS

On the assumption that there were no great variations in the properties of the steel in these specimens, the following conclusions may be drawn from the results of these tests:

1. The compressive tests of these welded bases for subway columns showed that they were practically as strong as the riveted bases having base plates.
2. The strength of these riveted bases without base plates was about 60 per cent of the strength of either the welded or the riveted bases having base plates.
3. For these welded and these riveted bases having base plates the bases were as strong as the H-section to which they were attached.
4. Hand strain-gage measurements on these welded specimens indicated that an increase in the thickness of the stiffener plates would make the bases stiffer.
5. With the base loaded on a span of 12 inches the stiffness of these riveted bases up to the yield point of the H-section was the same for the bases with base plates and without base plates.

WASHINGTON, May 28, 1930.

DIMENSIONAL CHANGES CAUSED IN GLASS BY HEATING CYCLES [1]

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ABSTRACT

In obtaining expansivity curves for a medium flint glass, samples of the glass were tested which had previously received one or another of several different heat treatments, and in these tests heating cycles were employed which made it possible to determine the magnitude of the so-called "permanent" changes in length which are caused either by the annealing or the "disannealing" which may result from the heat treatment imposed on the glass by the heating cycle employed. Annealing decreases the length and specific volume, while disannealing increases them. It is shown that these effects are related to certain ice-point shifts observed in thermometers, and to other effects sometimes observed in various types of glassware.

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I. INTRODUCTION

In common with a great many other materials glass will generally show, as a result of cyclic heat treatments extending over considerable temperature ranges, more or less permanent changes in its specific volume as well as in its form. In causing such effects it is not always necessary that the treatments reach temperatures in the so-called annealing and softening ranges since detectable changes in the specific volume (when determined at any one temperature) are at times produced by treatments which do not reach temperatures much above those of the atmosphere. The changes resulting at such low temperatures in well-annealed glass are, however, small and of little consequence when compared with those which are obtainable only at higher temperatures or which are the result of a failure of the glass to have reached the proper state of physico-chemical equilibrium when it was annealed. These dimensional changes produced by subjecting glasses to heating cycles approaching the annealing range are the subject of this investigation.

[1] An abstract of this paper was read at the Chicago meeting of the American Ceramic Society, February 4 to 9, 1929.

Certain of the well-known fluctuations and displacements common in the ice points of mercury-in-glass thermometers undoubtedly result from these changes in specific volume.[2] To introduce the subject of this paper more definitely, a discussion of these ice-point shifts and their possible causes will, therefore, be included here.

Of the ice-point shifts generally observed, part of the smaller ones (especially those occurring without heating above relatively low temperatures) may be traceable to changes in the shape of the bulb which result from variable strains. Strains introduced during the formation of the bulb and which remain effective because the annealing is insufficient may be of this character since they usually change slowly. Semipermanent or variable strains may also develop in an annealed bulb during the actual use of a thermometer in temperature ranges never reaching the annealing range if, for any reason, the expansivity and the possible specific volume change are not uniform over all parts of the glass or glasses used in making the instrument. These nonuniformities may arise from striae, the use of two different glasses, differences in the amount of working the glass receives when fused, or from temperature gradients during the fusions and annealing. Ice-point shifts from such causes should, however, generally be small and it would seem that they might with almost equal probability be either positive or negative. Furthermore, it would seem that while they can not be eliminated entirely a proper choice of glasses and suitable methods of producing both the glass and thermometers should make their significance negligible.

Another type of ice-point shifts which may occur and which result entirely from uniform changes in specific volume may be divided into two classes. As in the case of those ice-point shifts due to strains, the magnitude of those in the first class to be considered should be small and after being produced should usually decrease more and more slowly with time while the thermometer is held at a practically constant temperature near zero. On the basis of their assumed cause these shifts when observed at the minimum temperature of a cycle will, however, always have the nature of a depression and they will also develop, although their magnitude will usually decrease almost linearly with the extent of the range, after heating and cooling cycles which are within and consequently smaller than the usual 0° to 100° C. testing range. On extending the range to higher temperatures the observed depression should first increase and then decrease. General experience with glass, and other materials as well, suggests that these depressions result after heating and cooling cycles because the specific volume of even well annealed glass, after allowing for the change due to the normal expansivity, changes in a cycle which lags behind the causative temperature cycle impressed on the glass; that is, after a thermometer is heated very rapidly from 0° to 100° C., for example, and after its temperature becomes uniform and the expansion of the glass due to its normal expansivity is completed, the bulb, however, will still continue to expand slightly at a decreasing rate. This additional expansion, which continues at a constant temperature and which appears to be of sufficient magnitude and to proceed slowly enough even at 100° C. for observation in thermometers made from

[2] Young, Nature, **41**, p. 488; 1890. In this paper Young, besides ascribing the rise of the ice point to a volume change caused by the molecules assuming a position of greater stability, also refers to several interesting notes and articles on this subject by himself and others.

asses that are subject to relatively large depressions in this range, rresponds to a slow increase in the specific volume of the glass. n cooling to zero to complete the cycle this increase in volume will rsist for a relatively long time since, in general, all such readjustents proceed more slowly at lower temperatures. Work by a mber of investigators was required in the development of thermometer glasses which were not unduly subject to the depressions hich may be ascribed to readjustments of this kind, and thermometers now made from the best of these glasses seldom show, for cles between 0° and 100° C., depressions of more than one-tenth 1° C.

When, however, the temperature cycles are not confined to these latively restricted ranges such as 0° to 100° C., but are increased til temperatures near or within the annealing range are approached, e observed ice-point shifts become, in general, much larger. Such ifts are of the second class which may be ascribed to specific volume anges in the glass, and contrasted to the first class they may, pending on circumstances, consist of either depressions or elevaons with the latter being far more common in practical thermometry.

These differences between the two classes arise from the fact that e noticeable readjustments possible in different temperature ranges e different. Thus at 100° C., for example, the only noticeably tive readjustments in a glass previously held at 0° are generally l comparable to disannealing processes, although the state of the ass at 100° is not one of equilibrium for that temperature, but for me much higher temperature; that is, when a thermometer, for ample, is annealed and cooled all major readjustments which might oduce equilibrium at 100° C. cease to operate at any appreciable te long before this temperature is reached. Certain minor readjustents, however, continue through this point and until the glass is arer to, or reaches zero. On reheating, the minor processes are versed and disannealing results throughout a considerable range, G. ee footnote 3.) This effect alone is noticeable until some temerature range, G_1, well above 100° C. is reached where the major ocesses again operate at a noticeable rate and the annealing readstment with its usual decrease in specific volume is resumed. If e heating is continued until a range, G_2, is reached which is above e temperature corresponding to the equilibrium condition proced in the glass by the previous annealing treatment, the majority the annealing processes will be reversed, and a disannealing somehat similar to that at 100° C. with its usual increase in specific olume will again be the predominant effect. If instead of continug the heating, the thermometer had been held for some time at any mperature below G_1 and then cooled rapidly, an ice-point depression ould have resulted. Treating and cooling in the same manner from y point in G_1 would have produced an elevation, the magnitude of hich would depend on various factors. From G_2 such treatments ould again produce depressions.[3] All of these effects may be modied by, but they are not the result of, strains; and it is in fact only ose ice-point displacements that are not caused by strains and hich may be obtained only by heating to temperatures in and above

[3] In Figure 1 the region to the right of PQ contains the ranges G_2. Ranges G_1 are to the left of PQ and ere some boundary corresponding to S, but which will usually include more of the lower temperatures. anges G are to the left of PQ and below this rather indefinite boundary corresponding to S.

G_1 that correspond to the experimental results on changing th specific volume which are shown in this paper.

In regard to the magnitude of these particular ice-point displac ments it is well known that under some conditions shifts amountin to 30° C. or more are possible even when the heating cycles a extended to temperatures only moderately high. Since densi changes of corresponding magnitudes may be obtained by varyi the annealing schedules of most glasses it appears that, as indicate in the previous paragraph, these particular shifts are caused mainl by changes in the specific volumes of thermometer glasses. The fa that these large ice-point shifts are more often elevations than d pressions is merely a consequence of the ordinary practices follow in the manufacture and use of thermometers; that is, either th scales, and consequently the probable heating cycles to which th thermometers will be subjected when in use, extend to temperatur which are near or within the annealing ranges of the glasses witho actually reaching the effective temperatures [4] of the annealing trea ments previously given to the thermometers; or, these annealin treatments were entirely inadequate since they failed to establi those physico-chemical conditions which are reasonably stable at temperatures below the annealing range. Inadequate annealing of course, indefensible but the practice of somewhat overextendi the scales may in some very exceptional cases be justified. Th practice should, however, be avoided if possible and it should nev be followed without providing an adequate annealing which presum bly should be given just before filling and graduating the thermomet and at temperatures as near the top of the proposed scale as possibl Normally it would appear that an adequate annealing treatment f a thermometer is one which will produce a physico-chemical co dition corresponding closely to one of equilibrium for a temperatu not too far above the lower limit of the practical annealing rang This temperature corresponding to the equilibrium condition defined in footnote 4 as the effective annealing temperature of a annealing treatment and when a thermometer is heated to poin above it an ice-point depression will usually be observed, as previousl stated.

The fact that a thermometer can not be expected to give a satisfa tory performance if it is heated to temperatures which exceed the low limit of the annealing range is well known, but it does not appear t be so generally appreciated that this limit is considerably lower tha those temperatures which may be employed in giving a glass a reason ably thorough and for most purposes a sufficient annealing in reasonable time. The best means of determining for a given glass safe upper limit for the scale is, of course, to extend the heatin cycles imposed on a comparatively well annealed test thermomete of the glass gradually to higher and higher temperatures until th point is finally reached where a treatment of several hours at th maximum temperatures of the cycles begins to produce ice-poin

[4] The effective temperature of an annealing treatment may be defined as that annealing temperature which practically the same effect produced on the physico-chemical condition by the actual schedu employed might have been obtained through an annealing period at that temperaturre adequate to produ physico-chemical equilibrium and by a cooling rate such that no further annealing occurred during th cooling period. The resultant effective temperatures of ordinary annealing treatments may be either low or higher than the actual temperature employed. It is usually lower if the temoerature used is high in th annealing range and the cooling rate is low; while it is generally higher if the temperature employed is lo and the annealing period is short.

placements which just approach the specified tolerances for such fits.[5] That this apparently self-evident precaution is often neglected shown by the fact that many thermometers are graduated as far 50° or 100° C. into that more or less indefinite region termed the nealing range. Such thermometers on being used to register these h temperatures can scarcely be expected to meet successfully any sonable specifications.

That unwarranted requirements, such as this use of thermometers too high temperatures, are so often imposed on a glass when they ld in most cases be obviated merely by making a correct choice m the glasses available can only be explained by assuming that re exists in many quarters an insufficient knowledge concerning rtain important characteristics of this material. To aid in present- a clear conception of these characteristics it was planned some rs ago to undertake, in connection with the density determinations progress, an investigation which would involve a series of expan- ity measurements on several samples of a glass, each of which was have received previously a heat treatment considerably different m that of the others.

At that time a tentative diagram similar to Figure 1 was prepared an aid in choosing desirable treating temperatures and in predicting d interpreting the results of such tests. To some extent this gram followed the presentation used by Marchis [6] in his thesis on rmanent modifications of glass but with respect to detail it was sed chiefly on the experience gained from a study of the particular ss to be used in the tests, on a general knowledge of the changes ich are caused in the properties of glass by heat treatment, and on rtain generalizations arrived at after a consideration of the expan- ity measurements obtained by Peters, Cragoe, Merritt, and others.[7] Corresponding diagrams may be constructed for any property fected by the changing physico-chemical conditions in any material ving characteristics similar to those of glass.

This diagram (see fig. 1) with some modification is included in the esent article mainly because such diagrams have at times been very eful. Although it has certain patent defects, they can not be prop- ly remedied until more data are available. It is, however, sufficiently curate and elaborate to aid in the discussion of the results presented this paper.

II. EXPERIMENTAL METHODS AND APPARATUS

1. GENERAL CHARACTER OF THE GLASS TESTED

The glass chosen for these preliminary experiments was a medium nt, B. S. melt 494, that had been used in previous investigations [8] on e effect of heat treatment of the density, refractivity, etc. This oice was made because it was desired to compare the dimensional

[5] A limit so determined will usually be well below that which is determined by noting the temperature which the internal pressure from the gas over the mercury column causes the bulb to distend. As a matter fact in the G_1 range the two effects involved are of opposite sign. With a well annealed thermometer e G_1 shifts may all be smaller than a reasonable tolerance. In such a case, however, it is likely that the shifts will become excessive long before the depressions due to pressure become marked.

[6] L. Marchis Les Modifications Permanentes du Verre et le Déplacement du Zéro des Thermomètres, ris, 1898.

[7] Peters and Cragoe, B. S. Sci. Paper No. 393; 1920. Merritt, B. S. Sci. Paper No. 485; 1924. Peters, S. Sci. Paper No. 521; 1926.

[8] Tool and Hill, Trans. Soc. Glass Techn., **9**, p. 185; 1925. Tool, Tilton, and Hill, J. Opt. Soc. Am. & Sci. Inst., **12**, p. 490; 1926.

EXPLANATION OF FIGURE 1

Curve *PQ* represents the cooling curve (contraction per unit length) of a gl sample cooled so slowly that the glass follows its sequence of physico-chemi equilibrium conditions. At *P* a cooling rate of many degrees per second may relatively slow while at *Q* a degree in many years may be very rapid when co pared to the respective rates at which a glass that is removed to an appreci extent from the equilibrium conditions corresponding to these points will appro stability. Curve *PE* represents the curve of a sample cooled very rapidly fr 700° C. and from an equilibrium condition corresponding to that or higher te peratures, for example, small particles quenched from 700° C. in water. Fo time the rate of cooling caused by the quenching is insufficient to prevent s drift along *PQ*, but ultimately, near the temperature determined by the cross of the curve *R*, this drift ceases and the curve proceeds in the direction *E*. T increasing angle which a tangent to curve *PE* makes with *PQ* indicates t decrease in the drift as the temperature falls, and the slope of the straight port *E* represents the normal expansivity. Likewise, the remaining two solid circ represent water quenchings from the indicated temperatures and from equilibri conditions at these temperatures. The first temperature is slightly above t range of curve *R* and before taking the direction *D* indicating a normal expansiv there is a slight drift in spite of the rapid cooling caused by quenching; but t lower one being below *R*, the drift is inappreciable and the normal expansivity is followed.

If now a sample is quenched in air from 600° C. and from a condition rep sented by the open circle on the equilibrium sequence at that temperature, t physico-chemical condition of the glass will again drift considerably toward t equilibria of lower temperatures until the cooling curve approaches parallelism the direction *D* at the approximate position indicated by the curve *M*. On quenching from 500° C. with the glass in the condition indicated by the u lower open circle the drift is relatively slight and the curve soon becomes para to *C* without further drift toward *PQ*. Glass in equilibrium conditions cor sponding to the two remaining open circles will, on being air quenched from t indicated temperatures, follow, respectively, the normal expansivity slopes and *A* without any appreciable drift toward the equilibria of lower temperatur Samples of glass caused to follow curves *A* to *E* will have different densities; t following *E* having the least, and that following *A* the greatest. These limits intended to show the maximum variation attainable by practical means.

If the samples of glass *A* to *E* cooled as described are heated very rapidly; t is, at rates of the order obtained by water quenching, the expansion curv *AA'P* to *EE'P* will be followed. Samples *A*, *B*, and *C* will before crossing t curve *PQ* show no appreciable drift toward the equilibria of lower temperatur but will, after crossing and becoming considerably superheated, ultimately dr to the equilibria of higher temperatures. This drift, however, will not be app ciable until the region limited by *R'* is entered. The samples *D* and *E* will, on t other hand, after reaching the region *R* drift toward the equilibria at lower te peratures until *PQ* is crossed, then they will superheat relatively little bef drifting toward the equilibria of higher temperatures.

If, however, the samples *A* to *E*, inclusive, are heated at a much lower ra the expansion curves will be represented by *AA''* to *EE''*. In such a c samples *A* and *B* will show no appreciable drift toward the equilibria of low temperatures before *PQ* is crossed and, after crossing, the drift toward t equilibria of higher temperatures will be inappreciable only until the curve is reached. After crossing curve *S*, samples *C*, *D*, and *E* will drift towa equilibrium at lower temperatures until *PQ* is crossed. After crossing *PQ* slight superheating will occur, and then the drift toward the equilibria of high temperatures will begin.

To picture the significance of the family of curves to which *R*, *M*, and *S* a *R'* and *S'* belong, they may be considered as contour lines on the map of a vall of a mountain stream emerging from a narrow gorge at *P* and which gradua widens to a broad and relatively level plain between curves *S* and *S'*. T altitudes so indicated would represent the rapidity of the drift toward *PQ* sho by glass at different temperatures and in conditions corresponding to differe equilibria.

anges caused by the heating cycles imposed on the glass samples ring the expansivity tests with those results previously secured m the density changes observed in the same glass and already scribed in the papers cited.

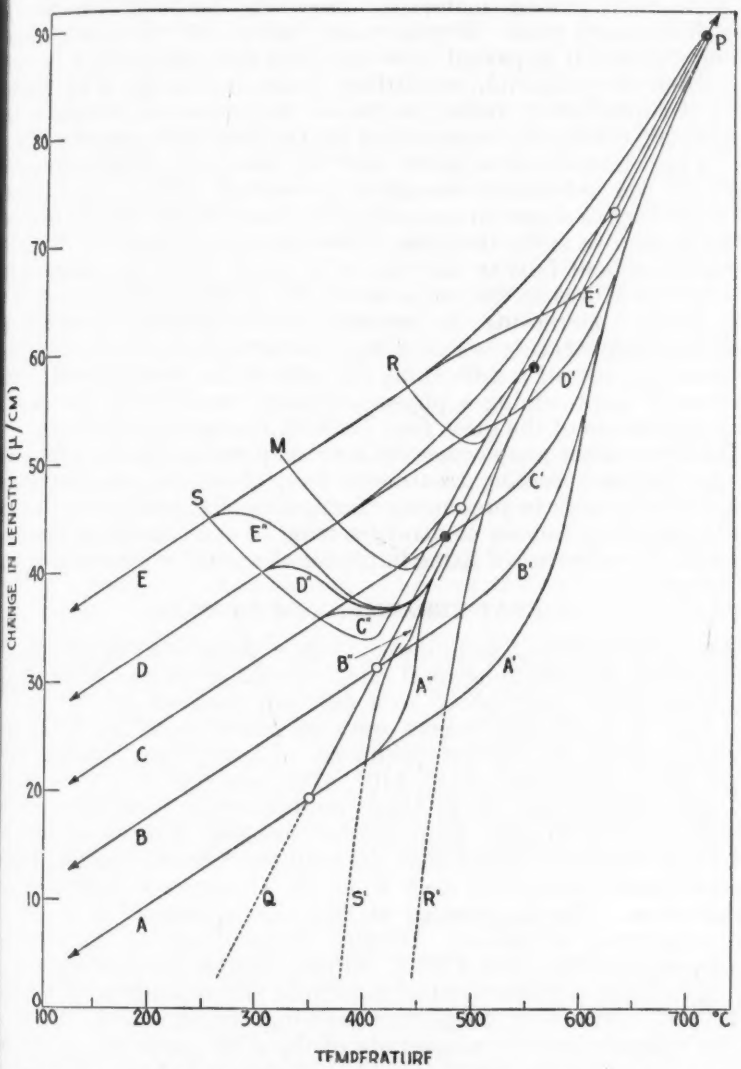

FIGURE 1.—*Diagram showing the effects of heating and cooling conditions on properties of glass*

The practical annealing range of this glass lies between the approxiste limits 370° and 470° C. At the lower temperature the time quired for a practically complete relaxation of stresses and the tablishment of a physicochemical equilibrium considerably exceeds month; while at the upper temperature it is of the order of one hour. om the previous investigations it had also been found that the

original cooling of the pot of glass had been such that the effec annealing temperature was between 400° and 410° C. It had been found that small pieces could be cooled in air at atmosph temperatures from all temperatures below 420° C. without introd ing permanent stresses materially exceeding the tolerances requ for well-annealed glass. Furthermore, below 400° C. a much slo cooling did not, it appeared, give the glass the opportunity to fo the course of equilibrium conditions (indicated in fig. 1 by the *PQ*) but compelled it, rather, to follow the courses of normal or expansivity conditions represented by the lines designated by *A* etc. From temperatures above 450° C., however, chilling in atm pheric air was not drastic enough to prevent all drift along *PQ* a was necessary to resort to quenching in water whenever, for exam it was desired to make the glass follow closely the line *C*. Even drastic treatment fails to halt the drift along *PQ* if the quenchi from temperatures in the range above the approximate limit 500 This need of increasing the severity of the chilling whenever quenching temperature is raised and whenever it is at the same proposed to prevent a drift along *PQ* reflects the rapidity with w the rate of approaching a physicochemical equilibrium increases the temperature of the glass rises through the annealing range.

The fixing of the more or less definite temperature limits given a for the different cooling treatments has, of course, no justifica except that it aids in presenting the results of experience. In o words, anything but an arbitrary setting of such limits is precl just as it is in the case of fixing limits for the usual or practical an ing range.

2. HEAT TREATMENT OF SAMPLES

Since the intention was to measure the expansivities and perma dimensional changes on several samples each of which should be condition which corresponds to a different position on the line nine lots of small glass pieces were prepared, each lot being l enough to make several test specimens. Eight treating temperat (360°, 370°, 390°, 400°, 420°, 440°, 470°, and 620° C.) were ch and the heating periods at these temperatures varied from a minutes at 620° to more than one and one-half months at 360°. had previously been found that the required treating period coul approximately halved for each 8° or 10° C. increase in the trea temperature. The lot treated at 620° was quenched in water, remainder were air chilled. Despite the smallness of the pieces lots treated at 620° and 470° C. drifted during the first part of cooling toward physicochemical equilibria corresponding to temp tures well below their respective treating temperatures. With higher temperature the magnitude of the drift probably approa 100° C., but with the lower (470° C.) it was much less. For the of the samples it is believed the drifts were inappreciable. It found, however, that the treatment given at 360° C. was too sho reduce the glass completely to equilibrium at that temperature.

3. PREPARATION OF TEST SPECIMENS

As the present investigation was more or less preliminary, variati in the size and shape of the test specimens were tried. The usual shape, however, was that of a pyramid whose base was so

it rested on three well-separated feet, thus supplying the stability ired of a separator in a sensitive Fizeau interferometer. The sur- s of the feet and the apex were smoothly rounded so that there d not be, at the higher temperatures, an undue deformation at points of contact between the specimens and the two fused quartz s used in the interferometer.[9] In each test a set of three such mids all having practically the same height were, of course, needed rve as separators in supporting the upper plate at the desired nce above the lower one. The final height adjustments required ve suitable interference bands for expansivity measurements by method have been described in sufficient detail by C. G. Peters his associates in the articles cited. The height of the pyramids at different times ranged between 1 and 5 mm, and was in every carefully measured on a special disk anvil micrometer. In gen- the pyramids with broad bases and relatively short altitudes gave most consistent results; presumably because of two reasons—their ter stability and the closer adherence of their temperature to that e bottom interferometer plate which, as described later, was used etermine the temperatures.

4. THE FURNACE

he interferometer system formed by the quartz plates and these midal test specimens was heated and cooled during the expansi- measurements in a tubular electric furnace similar to that ribed by Peters and Cragoe. A helix of aluminum tubing buried he thermal insulation and surrounding the heating coil consti- d, however, one modification. Through this tube a flow of some or liquid could be used to maintain the desired rate of cooling. ther modification consisted in replacing the customary porcelain containing the interferometer by a thick-walled one of aluminum. s cup served better to equalize the temperatures of the interferom- system. The introduction of these aluminum parts restricts use of the furnace to temperatures below 600° C., since the ting point of aluminum should not be too closely approached. other respects these aluminum parts proved satisfactory, and higher temperatures other metals are available. The heating cooling rates employed in the tests recorded here approximated er minute.

5. THE TEMPERATURE MEASUREMENTS

wo methods of determining the temperature were used. In the , a thermocouple with its hot junction in contact with the base he aluminum cup containing the interferometer was employed in usual manner. This served mainly as a control of the heating s, but it also gave a check on the second method particularly n the temperature was being held constant. The second method sisted of using the lower interferometer plate [10] as a "refraction mometer" and was depended upon to give a more accurate rmination of the actual temperatures of the test specimens, e they were in direct contact with this plate. In reference to this

ers and Cragoe, B. S. Sci. Paper No. 393; 1920. Merritt, B. S. Sci. Paper No. 485; 1924. Peters, Sci. Paper No. 521; 1926. Merritt and Peters, J. Am. Cer. Soc., 9, p. 327; 1926.

his plate was designed and calibrated for this purpose by Mr. Merritt, who plans in the near future cribe the method more fully.

plate it will suffice to say that its thickness and the relative inclination of its surfaces were such that it gave a satisfactory set of straight interference fringes which shifted approximately one fringe for each 5° or 6° change in temperature. As the movement of these fringes was at all times very regular throughout their length, and since a shift can be estimated to a tenth of a fringe with considerable accuracy, the precision of the temperature determinations was of the order of a half degree. If desired, the top plate may be so designed that a part of it may also be used as a refraction thermometer. In this way the axial temperature gradients existing in the space containing the test specimens may be determined; but the number of fringe systems requiring practically simultaneous attention is then such that a chronograph or other suitable system would be desirable for recording the passage of the fringes.

6. THE MEASUREMENT OF FRINGE DISPLACEMENTS

The shifts of the fringe system of the bottom plate and of that of the air wedge determined by the lengths of the test specimens between the two plates were determined by means of the usual equipment which is described in the articles cited. With the exception of a few cases where the test specimens were so tall that the air fringes moved very rapidly past the reference point on the top plate and in such numbers that to have recorded all of them would have been too laborious, the time of practically every such passing of a whole fringe was recorded. As each air fringe count was recorded, the number and fractional part of the refraction thermometer fringe which passed the reference point up to that time was also recorded. When the test specimens were relatively small or the temperature was being held stationary it was occasionally considered advisable to increase the number of observations on the air fringes beyond that of the whole bands. The labor required in recording the increased number of observations is compensated for by the advantage gained when it is found necessary to correct any count which proves to have been erroneous because of the accidental omission of a whole band and also by the greater certainty regarding the trend of the curves in graphical representations of the data. Furthermore, any instability on the part of the interferometer system is also more readily detected by using a larger number of points.

7. THE HEATING CYCLE

The upper limit of the heating cycles was chosen with the special purpose of keeping the glass at temperatures where it would not deform appreciably under the weight of the top plate. At the same time it was necessary for the chief purpose in view that this limit should be in the range where a physico-chemical equilibrium would be practically reached in a few hours if the time for procuring the data on a complete cycle was not to be too long. Preliminary tests showed this limit to be both safe and convenient when between 440° and 445° C., since at this temperature a large portion of the dimensional changes due to physico-chemical processes were completed within two hours although appreciable deformations were not detected after the heating had been continued for several hours. The heating cycle, therefore, consisted of heating the interferometer

system, formed by the two plates and three pyramidal spacers all contained in the aluminum cup, at approximately 3° C., per minute from room temperature to 443° C., holding it there until the expansion due to physico-chemical changes appeared to be complete, and then of cooling it to the starting temperature at approximately the same rate. At the end of such a run the glass spacers were, in general, either longer or shorter,[11] depending on the initial condition of the glass. If the effective treating temperature corresponding to this initial condition was below 443° C., the length of the spacers was increased by the cycle; if it was above, the length was decreased. The magnitude of these changes is controlled chiefly by this difference between the initial effective treating temperature and the holding temperature of the cycle, but it will naturally be reduced if the holding period is insufficient and will be somewhat affected by the changes which progress during the cooling. To insure against insufficient holding periods a second, and sometimes a third, run was made.

III. EXPERIMENTAL RESULTS

All details, such as the formula required, the corrections which must be applied because of the air density changes, and so on, which are involved in converting the fringe displacements caused by the changing altitudes of the pyramidal spacers into changes in length per centimeter have been sufficiently described in the articles mentioned above. Figures 2 to 7 represent graphically the changes in length with temperature which were obtained for the differently treated samples. To make sure that the curves shown represented with sufficient fidelity the expansions and contractions which should result from the previous treatments of the samples two or more sets of pyramids from each of the nine lots were tested. Not infrequently there occurred during these runs (usually after the first heating) certain small abrupt fringe displacements which appeared to be in nowise related to the temperature of the glass, and although their combined magnitudes seldom materially affected the general result of any run their occurrence did make repetitions of the tests even more desirable. Such repetitions revealed that these abrupt displacements were entirely accidental and that in most cases they could be either compensated for by taking into account the two or more sets of observations or entirely neglected in deciding upon the most probable trend of the expansion curves. Since the curves in the figures lie so close together, it was found impossible to show the points corresponding to each individual observation and consequently only the smooth trend is given. This procedure does not make these displacements evident, but they were none the less definite.

With regard to the cause of these accidental effects, they seemed to be induced chiefly by the difference in the expansions of the glass pyramids and the fused quartz plates in contact with them. The effect of this difference was probably exaggerated by the slight temperature differences existing between the top and bottom plates. So long as the specimens slipped freely on the plates the differential expansion caused little trouble; consequently, most of the first heat-

[11] Schonborn, Sprechsaal, **61**, p. 99; 1928. This author has published considerable data on the shortening of drilled glass rods.

ing after the exposure of the interferometer to ordinary atmospheric conditions was accomplished without any marked irregularities in movement. These were likely to appear, however, as soon as the heating had cleared away the possible lubricating films of gases, etc. They were, therefore, presumably caused or accentuated by a gradual tilting of the spacers when these did not slip properly on the plates.

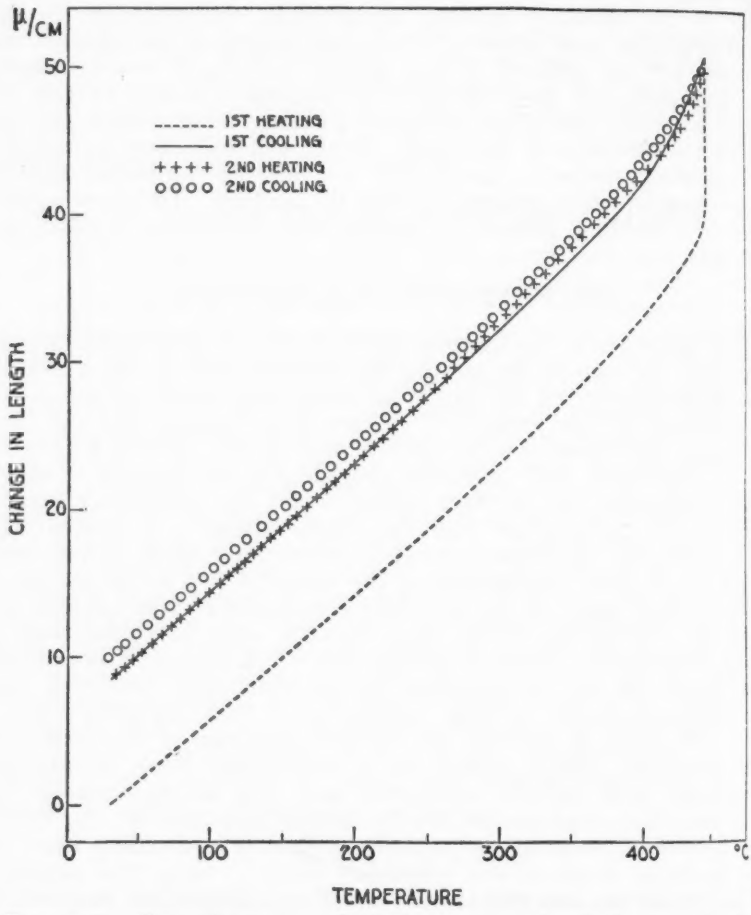

FIGURE 2.—*Expansion curves obtained on a sample of glass previously treated at 360° C. for 47 days and cooled in air*

First cycle.—Heating curve indicated by broken line, cooling curve by continuous line. Held at maximum temperature approximately one hour.

Second cycle.—Heating curve indicated by crosses, cooling curve by circles. Held at maximum temperature approximately 15 minutes.

The unit μ (one micron), used in the ordinates, is 10^{-4} cm.

This action changed for a time the apparent rate of expansion which was in most cases ultimately compensated for by a return of the interferometer system to stability. At times this return would be abrupt; at others it was gradual, often causing the apparent expansion curve to show changes in slope which might be erroneously interpreted as indicating some change in the glass. These erratic

effects are apt to be very troublesome in obtaining cooling curves whenever the heating has been pushed to temperatures where the spacers adhere[12] slightly to the fused quartz plates. This occurs to some degree with smooth plates, but much more often and to a greater extent with plates which have become somewhat roughened and thus allow the glass to fit into and grip their surfaces.

The curves in Figure 2 show essentially how the glass of the sample previously treated at 360° C. follows, on the first heating, a normal

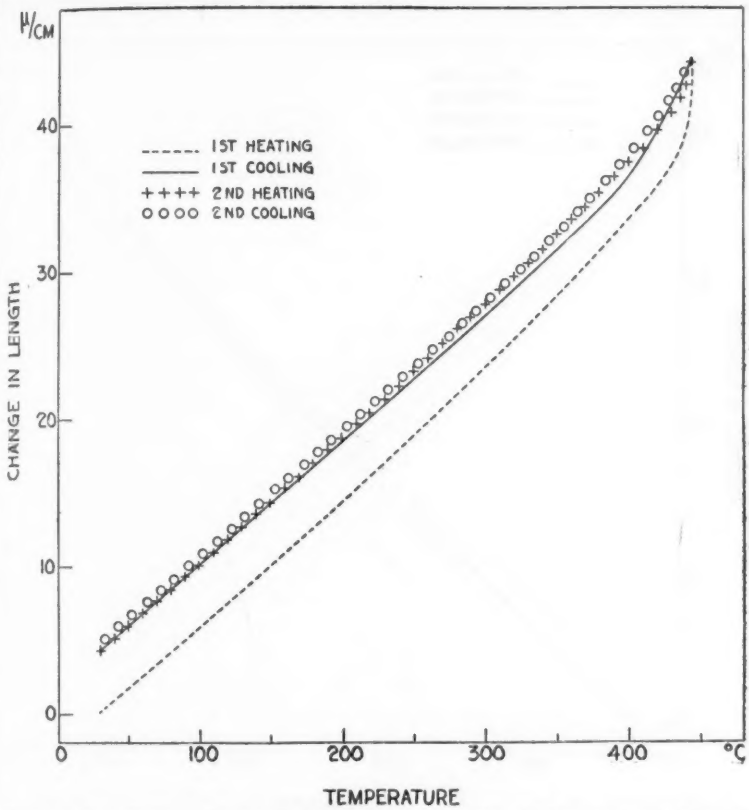

FIGURE 3.—*Expansion curves obtained on sample of glass untreated except for the usual cooling in the pot*

For description of cycles see remarks under Figure 2 and in text

expansivity curve (similar to *A* and *B* in fig. 1) until the line corresponding to equilibrium conditions (*PQ* in fig. 1) is crossed. This crossing probably occurred shortly after reaching 370° C. because it was found that the treatment at 360° C. had not been long enough to produce more than the effect of a completely effective treatment at 370° C. This would mean, in view of the rate of heating employed, that shortly after reaching 370° C. (possibly near 400° C.) the apparent expansivity should increase somewhat because of a drift toward equilibrium. This drift, which in this case is not very marked until 420° C. is reached, signifies the introduction of a "permanent"

[12] Klemm and Berger, Glastechnische Berichte, 5, p. 405; 1927.

increase in volume. Although the temperature was maintained practically constant at the holding temperature, 443° C., the increase in length during the holding period was almost a sixth of the total change which took place due to normal thermal expansion between room temperature and this holding temperature.

Considering the low internal mobility of the glass and its resultant slow change toward equilibrium at this and lower temperatures, the rate of cooling, 3° C. per minute, is rapid and, consequently, the curve representing the first cooling shows only a relatively small

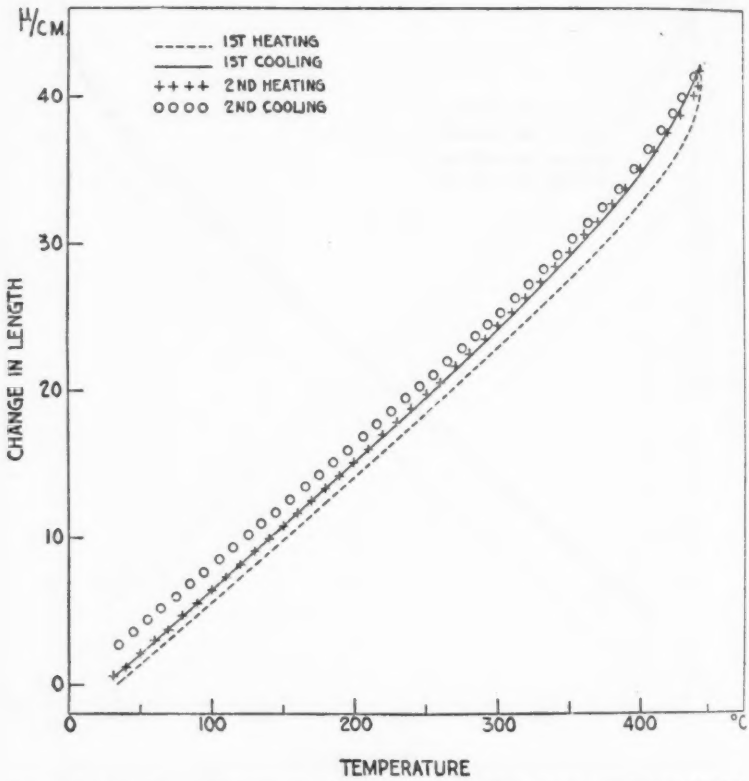

FIGURE 4.—*Expansion curves obtained on sample of glass treated at 420° C. for five days and cooled in air*

For description of cycles see remarks under Figure 2 and in text

return drift toward any equilibrium for a lower temperature. As a result the major part of the change at the holding temperature was retained until room temperature was reached and this change may, therefore, be termed a permanent one, although it is no more permanent than the opposite change which of necessity preceded it during the annealing treatment of the sample at 360° C. The second cycle of heating, holding, and cooling produced a slight additional increase which was mainly due to the fact that the first holding period was too short. In fact, experience would indicate that when starting with the glass in the condition of this sample both these cyclic treat-

ments combined were insufficient to produce more than possibly nine-tenths of the change which would normally follow the establishment of complete equilibrium in this particular sample at 443° C. To attempt to gain the whole change would, however, be too tedious in an investigation of this sort. This is true since the process of approaching equilibrium is aperiodic; that is, it proceeds endlessly but at a continually decreasing rate.

Figure 3 represents the results obtained on specimens from the untreated sample. This glass was in a condition corresponding to

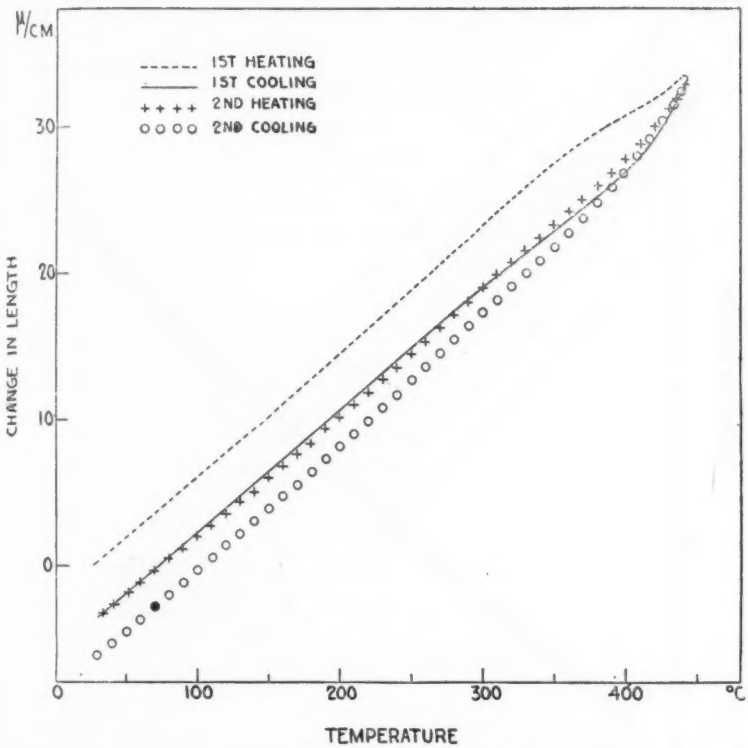

FIGURE 5.—*Expansion curves obtained on sample of glass treated at 470° C. for three hours and cooled in air*

For description of cycles see remarks under Figure 2 and in text

equilibrium at a temperature slightly over 400° C., consequently, in this case also a noticeable increase in the rate of expansion did not occur until 420° was reached. The change occurring at the holding temperature was not so great as in the previous case, but, as before, the second cycle increased this permanent change slightly.

The next case was of interest because it had been previously estimated that the treatment involved in these heating and cooling cycles of the expansivity tests should be approximately the equivalent of an annealing treatment which would produce equilibrium at 420° C. This appears not to have been entirely correct, since the curves in Figure 4 (see also curve *E*, fig. 7) appear to show that 430° C. would

have been a closer estimate, a conclusion supported by the curves obtained for the sample treated at 440° and represented in Figure 7 by curve *C*. In Figure 4 the permanent change in length after the second heating was unduly large in comparison to that found after the first. This may be due to either or both of two causes—either the holding period of the first cycle may have been too short or there may have been a slight difference between the holding temperatures. The latter appears more probable, since to stop a steady rise in tem-

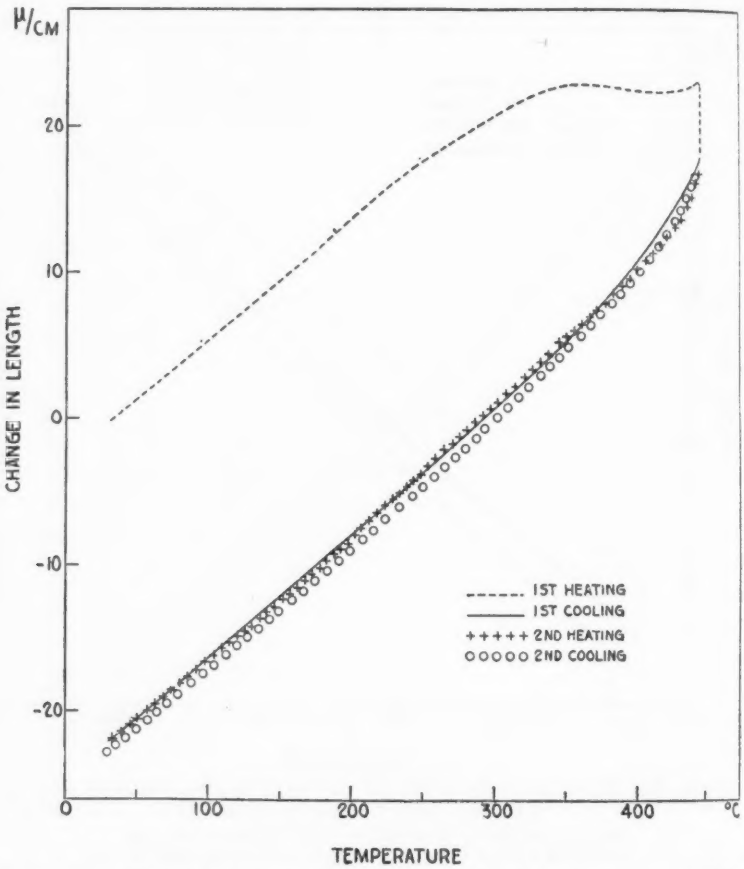

FIGURE 6.—*Expansion curves obtained on sample of glass treated at 620° C. for 15 minutes and quenched in water*

For description of cycles see remarks under Figure 2 and in text

perature of 3° C. per minute abruptly at a given point without error requires, to say the least, considerable manipulative skill.

In Figure 5, which represents the results obtained on the sample treated at 470° C., the condition was reached, as was also the case of that treated at 440° C., where there was no actual crossing of the equilibrium sequence PQ (which if incorporated in this figure should lie to the right) by the expansion curves; that is, the equilibrium temperature established by the treatment of the sample was above the

holding temperature employed in these expansivity tests. In consequence the specimens from this sample suffered permanent contractions after both cycles. The contraction began at temperatures as low as the 350° C., on the first heating. In measurements on samples such as these which have been chilled rather severely in the attempt

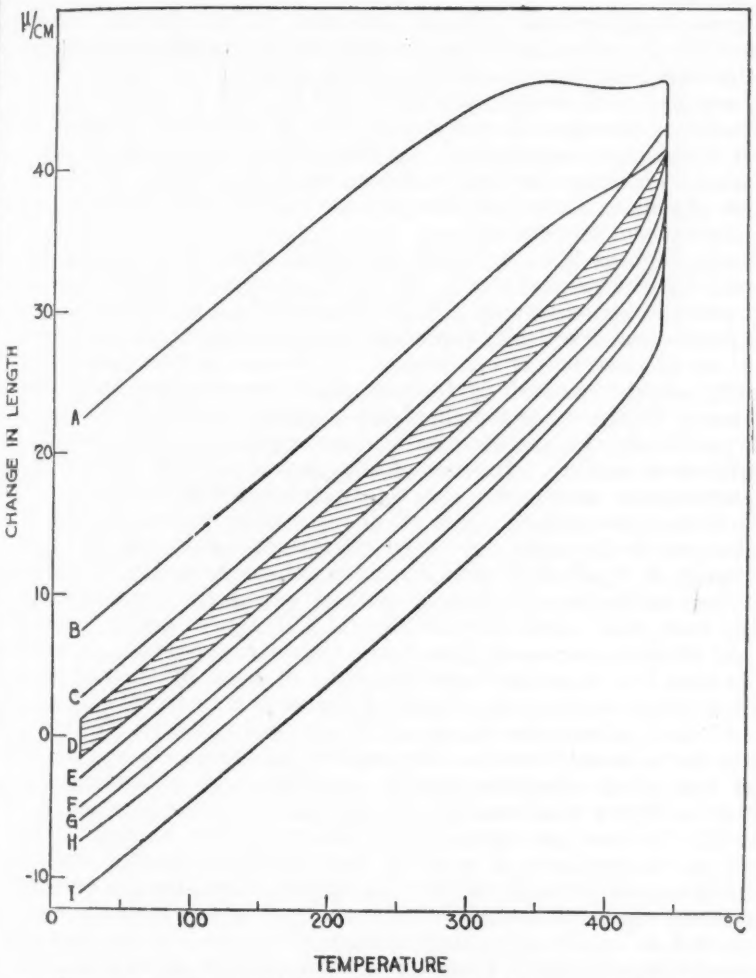

FIGURE 7.—*Composite diagram of the expansion curves obtained*

Curves *A*, *B*, *C*, *E*, *F*, *G*, *H*, and *I* represent the first heating curves obtained on the samples previously treated at 620°, 470°, 440°, 420°, 400°, 390°, and 370° C. The sample corresponding to curve *E* was untreated. The first cooling curves coincide roughly with the edge of the shaded portion *D* nearest the corresponding first heating curve. The cooling curves of the second cycle coincide approximately with a median line through the shaded portion.

to obtain a condition at room temperature which will correspond to a position well up on the sequence PQ (see fig. 1) mechanical strains introduced by this treatment will usually be quite troublesome, since they add considerably to the instability of the interferometer system and produce small disturbing displacements similar to those previously

discussed. The effects produced by the strains, however, are almost as likely to cause an apparent expansion as they are an apparent contraction. Furthermore, if the test specimens are properly designed, these apparent length changes are, in general, very much smaller than the permanent contractions due to changing equilibrium conditions.

Figure 6 representing results obtained on the sample [13] quenched from 620° C., shows a still more pronounced permanent contraction. In this case it appears to have begun below 250° C. on the first heating and reached such proportions near 350° C. that it overshadowed the normal expansivity and changed it into an apparent negative coefficient for rising temperature. At the holding temperature this contraction continued for some time, and practically stopped only when physico-chemical equilibrium at 443° C. was, from a relative standpoint, not far removed.

From Figures 2 to 6 it will be noted that, as indicated by the curves for the second cycle, the total change in length caused by the normal expansivity on cooling from 443° C. to room temperature was in all cases practically the same; that is, it was in the neighborhood of 41 or 42 microns per centimeter. This contraction caused by the cooling of the second cycle over this temperature range should obviously be the same for all of the samples, provided the first cycle was practically sufficient to produce in every case a normal equilibrium condition at 443° C. In view of this, it was possible with very little adjustment to construct a diagram which includes curves for all the various samples and in which all of the cooling curves for the second cycles practically coincide. Figure 7 is such a diagram and in it the curves *A*, *B*, *C*, *E*, *G*, *H*, and *I* correspond, respectively, to the results obtained on the first heatings of specimens from the samples treated at 620°, 470°, 440°, 420°, 400°, 390°, and 370° C. Curve *F* corresponds to the original untreated glass, while the shaded portion, *D*, is so outlined that it is bounded in the majority of cases by the curves of the first coolings and contains those of the second heatings and coolings. It will also include the curves of all succeeding cycles so long as the particular schedule used in these tests is followed. It will be evident that this whole diagram may be considered as occupying an area which in Figure 1 is bounded approximately by the lines *A*, *A''*, *C''* and *C*. It must be remembered, however, that Figure 1 was constructed on the basis of more or less indefinite heating and cooling conditions and through the use of assumed values for the constants of the glass; that is, it is merely a generalization in which the constants were chosen mainly according to convenience so long as they did not appear unreasonable. Consequently, a perfect correspondence cannot be expected, and for that reason the agreement obtained seems striking.

IV. CONCLUDING DISCUSSION

The permanent changes in length noted after the test specimens from the various samples had been subjected to these treating cycles are indicated in Figure 7 by the ordinate differences at 20° C. between a central position in the shaded portion, *D*, and the curves *B*, *I*, etc. Taking into consideration all the determinations obtained on the

[13] This was part of the quenched sample used in a previous investigation, the results of which are being prepared for a future publication.

samples treated between 370° and 470° C., it was found that the indicated total permanent change in length which could be produced in this particular glass between these treating temperatures was between 17 and 18 microns per centimeter. While the magnitude of such a change can not be determined by this method with the precision reached when the corresponding volume change is obtained from the determinations required in careful density measurements, it should still approximate the linear change which may be computed from these more precise volume determinations and which had previously been found to be very nearly 16 microns [14] per centimeter for a difference of 100° C. in the treating temperatures. That this more precise value is lower than that above is not surprising, since the density changes were determined on large samples which at high treating temperatures allow, because of their size, a relatively larger drift along the equilibrium sequence than that which was permitted by the smaller and more easily quenched samples used for this investigation. One factor leading to greater precison in the density measurements arises from the fact that changes in shape have no effect on such measurements while they always present difficulties in linear expansivity tests.

This medium flint is, of course, not a thermometer glass, although tests have shown that its annealing range approximately coincides with the lead glasses often used in thermometer stems. For that reason it is interesting to compute the ice-point displacements which might be expected if both the bulb and stem were made from it. Since the linear change per degree is approximately 1.6×10^{-5} it is seen that in round numbers 5×10^{-5} may be considered as the volume change per degree change in the effective annealing temperature. As the differential expansion per °C. for this glass and mercury would be about 1.5×10^{-4}, this means that for every degree reduction in the effective annealing temperature there will be a rise of ⅓° C. in the ice point. If such a thermometer were carefully annealed at 400° C. before being filled and calibrated to that point, it would later, on being held for a few hours at 390° C., which is presumably a safe point on the scale, considering that it extends to 400° C., show a rise which might well exceed any tolerance ordinarily required. Actual tests have shown that some of the 400° C. thermometers on the market behave in just this manner. In fact, holding them in the range between 380° and 390° C. for two weeks will, occasionally at least, produce displacements which exceeds +10° C. If the ice point is determined both before and after use at these high temperatures, such a change, since it occurs slowly is, of course, not so important and becomes a mere nuisance. As a matter of fact, however, these thermometers should not be graduated higher than 350° C.; and, moreover, not to that point unless they have been so carefully annealed that the effective treating temperature has been brought well below 400° C. Reducing the effective annealing temperature below the upper limit of the scale is of little benefit in the case of such thermometers if they are graduated to 400° C., because if this temperature has been reduced to 380° C., for example, any extended use of them at 390° C. will then produce a considerable ice-point depression.

[14] The approximate values for the change in density per ° C. decrease in the effective annealing temperature, the density and the linear expansivity are respectively, 16×10^{-6}, 3.35 g/cm³, and 0.9×10^{-5} per ° C. See Tool and Hill, Trans. Soc. Class Tech., **9**, p. 199; 1925.

Using a low annealing range glass of this sort in the stem and glass with the same expansivity but a higher annealing range in the bulb in order to reach 400° C. has possibly, in relation to this particular type of ice-point displacement, some advantages but is also likely to cause difficulties of a somewhat different character. These will arise from the fact that it is impossible to anneal both glasses thoroughly, since to properly anneal the bulb would endanger the stem through softening; while if the stem alone is well annealed there will be throughout the annealing period a clamping effect upon the bulb at the line of fusion. This effect caused by the greater shrinkage of the stem will be difficult to eliminate if it is introduced by annealing at low temperatures; and as soon as the thermometer is used at temperatures above the effective annealing point of the stem, the consequent disannealing will reduce the effect and it may even introduce a temporary spreading effect. Such distortions of the bulb would naturally lead to erratic results, especially if the thermometer is employed at too high temperatures.

These particular clamping and spreading effects which appear at junctions and which result, during heating and cooling, from differences in annealing temperatures, have a very wide significance wherever two or more glasses, which may even be only slightly different, are required in fashioning an article. In fact, it is evident that besides the normal expansivities two other factors, the expansions (or contractions) caused by changes in physico-chemical equilibrium conditions and the annealing ranges, must be considered whenever two glasses are fused together. Even in an article made entirely of one glass the first of these two factors may assume considerable importance as a cause of breakage if the heat history of all parts of the article has not been the same and particularly if the whole article is not properly annealed subsequent to its fabrication. This should be evident from the curves presented, since they show that the "permanent" change may easily exceed a sixth of the normal thermal expansion incurred in heating the glass from room temperature to the annealing range.

It will be noted that the normal expansivity of this glass as indicated by the slopes of the curves below the annealing range does not appear to vary greatly and that changes in the heat treatment do not affect it materially. What might seem to be a large variation at the higher temperatures has been shown to be due mainly to the "permanent" dimensional changes which have been the subject of this article and which are not related to the true expansivity of the glass. Any change in the equilibrium condition of the glass should cause, however, some change in the true expansivity, but normally this change in the expansivity is not likely to be more than a few per cent. In fact, it is to be presumed that the total effect which any such change in this coefficient might cause in cooling from the annealing range to room temperature would normally be less than the "permanent" change in length which is possible as a result of changing the equilibrium temperature through a relatively small interval.

WASHINGTON, June 19, 1930.

ACCURATE METHOD OF MEASURING TRANSMITTED WAVE FREQUENCIES AT 5,000 AND 20,000 KILOCYCLES PER SECOND

By E. L. Hall

ABSTRACT

The measurement of the frequency of a radio transmitting station offers a convenient means of intercomparison of frequency standards. While there have been several articles published dealing with station frequency measurements, these have, for the most part, considered frequencies in the broadcast band or lower. This paper describes a method of measuring station frequencies applicable to any frequency, but dealing primarily with frequencies of approximately 5,000 and 20,000 kc. A high order of precision is obtained by the use of harmonics and audio-frequency beat notes. Most of the units of the equipment employed have been previously described in connection with other applications.

The measurement of the frequency of a radio transmitting station offers a means of intercomparison of the frequency standards of two or more laboratories, which may be in different countries, and of calibrating secondary frequency standards in various laboratories. The above applications have been used with increasing accuracy as improvements in radio apparatus and technique of measurement have become available. However, the accuracy obtainable in the intercomparison of two frequency standards in this manner may be surprisingly good if suitable measurement methods are chosen, as will be shown later.

In 1923 and 1924 simultaneous measurements were made upon the transmissions of some of the transoceanic telegraph stations by two European laboratories and the National Bureau of Standards. The agreement was of the order of 0.2 per cent.

The method of measurement described by Royden,[1] using a frequency meter, is stated to readily give an accuracy of 0.1 per cent. While the frequency range covered is not stated, measurements at 15 and 20 kc are mentioned.

A year ago the frequencies of the European broadcasting stations were being measured with an accuracy of 0.02 per cent,[2] using the apparatus and methods described in papers by Braillard and Divoire.[3, 4, 5] Refinements in the method not usually used were said to increase the accuracy to a few thousandths of 1 per cent.

Frequency measurements upon broadcasting stations as described by Bogardus and Manning [6] were made with an accuracy of about

[1] George T. Royden, The Frequency Checking Station at Mare Island, Proc. I. R. E., **15**, pp. 313-318; 1927.
[2] W. H. F. Griffiths, Accurate Wavemeter Design, Wireless World (London), **26**, p. 113; January 29, 1930.
[3] Braillard and Divoire, The Exact illand Precise Measurement of Wave Length in Radio Transmitting Stations, Exp. Wireless & Wireless Engineer (London), **4**, pp. 322-330, 394-401; 1927.
[4] R. Braillard and E. Divoire, How Broadcasting Wave Lengths are Checked. A Description of the International Listening Station at Brussels, Wireless World, **22**, pp. 219-222; 1928.
[5] R. Braillard and E. Divoire, Measurement of Wave Lengths of Broadcasting Stations, Exp. Wireless Wireless Engineer (London), **6**, pp. 412-421; 1929.
[6] H. L. Bogardus and C. T. Manning, The Routine Measurement of the Operating Frequencies of Broadcast Stations, Proc. I. R. E., **17**, pp. 1225-1239; July, 1929.

a hundredth of a per cent. The same order of accuracy is obtained by the method used in Italy by Pession and Gorio.[7]

Radio transmitting sets of a few years ago had no means of accurately controlling the frequency such as is now possible with piezo control which is maintained at a constant temperature. If a radio transmitting set can be relied upon to maintain its frequency quite accurately, it is no longer necessary that simultaneous frequency measurements be made in order to obtain accurate frequency comparisons. There are probably very few technicians accustomed to making frequency measurements of high precision, who would guarantee to make such measurements at definitely prescribed times because of various kinds of interference which invariably occur at such times. This is true at least in a radio laboratory where several may be engaged on various kinds of testing work at the same time and electric motors and other apparatus may be producing interference. However, if the transmitting set remains constant, measurements can be made as convenient and consistent results can be obtained.

Some months ago the bureau undertook to measure the frequency of the transmitted wave of NKF, Bellevue, D. C., which was approximately 20,085 kc. This transmitting set is piezo-controlled by a quartz plate with a frequency of approximately 2,510 kc. Successive frequency doubling stages are employed. During preliminary measurements an antenna was temporarily connected in to the 5,000 kc stage and then to the 10,000 kc stage, as well as to the final stage. The transmission could not be picked upon on the 10,000 kc transmission, presumably because the bureau was within the skip-distance for this frequency and the ground wave was not of sufficient strength. As both the 5,000 and 20,000 kc transmissions could readily be picked up, it was thought desirable to have both these frequencies transmitted and use the measurements on one frequency as a check on the measurements at the other frequency. This was accomplished through the courtesy of Dr. Taylor and his associates at the Naval Research Laboratory.

The measurements here considered have been made upon special transmitted signals, the part used in measurement consisting of a long dash. While the method can be employed upon the keyed signal of a station, yet it loses its great precision in such a case because it is difficult, if not impossible, to match a steady note precisely with an intermittent or broken note. Experience has shown the necessity of an identifying signal, such as the station's call letters, but these should be kept to a minimum, and the dashes for measurement purposes made to predominate.

Most of the apparatus used in the measurements has been described in other papers.[8, 9, 10] The paper[9] on testing piezo oscillators states that the method described is also applicable to the measure-

[7] G. Pession and T. Gorio, Measurement of the Frequencies of Distant Radio Transmitting Stations, Proc. I. R. E., **17**, pp. 734–744; April, 1929, and Sulla Misura Della Lunghezza D'Onda, Pession and Gorio, Elettrotecnica (Italy), **15**, pp. 524–530; 1928.

[8] E. L. Hall, A System for Frequency Measurements Based on a Single Frequency, Proc. I. R. E., pp. 272–282; February, 1929.

[9] E. L. Hall, Method and Apparatus Used in Testing Piezo Oscillators for Broadcasting Stations, B. S. Jour. Research, **4**, pp. 115–130; January, 1930; also as Research Paper No. 135, obtainable from Superintendent of Documents, Government Printing Office, Washington, D. C., for 10 cents. Proc. I. R. E., **18**, pp. 490–509; March, 1930.

[10] N. P. Case, A Precise and Rapid Method for Measuring Low Frequencies, B. S. Jour. Research, (RP195), p. 237, 1930; and the Proc. I. R. E.

ment of station frequencies. Since the paper was prepared, the Bureau has obtained a very accurate primary standard of frequency, similar to that described by Marrison.[11] The frequency measurements are based upon this new standard rather than upon the standard mentioned in the previous reference.[9]

The method of measurement is the familiar one consisting of tuning a receiving set to the frequency of the station to be measured, adjusting a radio-frequency generator to the same frequency or some harmonic of it, and measuring the frequency of the generator. The frequency relation between the generator and the receiving set being known, the frequency of the signal is readily obtained.

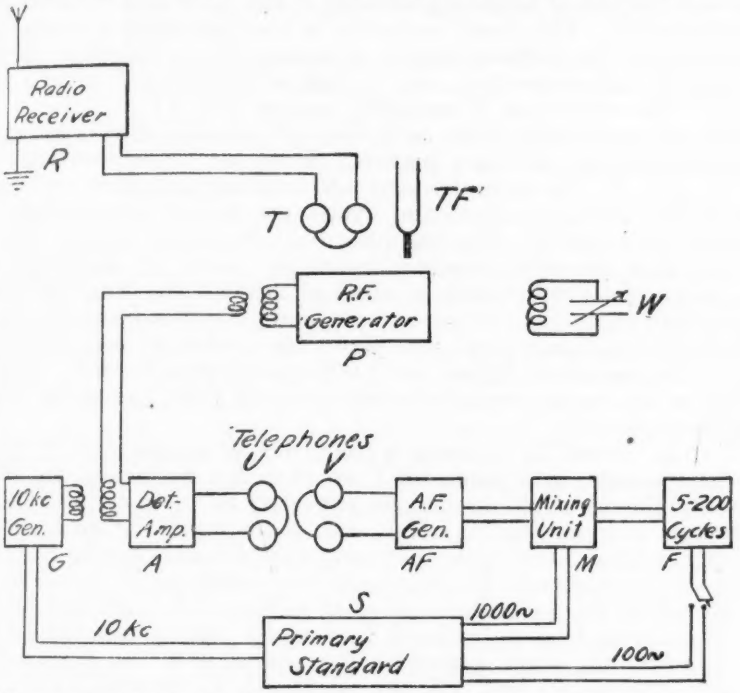

FIGURE 1.—*Schematic diagram of apparatus used in measurement of station frequencies in terms of the primary frequency standard*

In order to explain the refinements making for increased precision and accuracy in the measurements to be described, reference is made to Figure 1. The radio receiver R is adjusted to the desired station signal, as for example, 5021 kc, and left in a nonoscillating condition. The generator P is then adjusted to "zero beat" with the radio receiver, and a reading taken upon the frequency meter W. Generator P is then adjusted away from "zero beat" until beats are obtained by matching with the note from a tuning fork TF, which is held in the hand and struck with a small mallet as desired. A second reading is taken at this time upon the frequency meter W, the readings of which are used in recording the direction from zero

[9] See footnote 9, p. 648.
[11] W. A. Marrison, A High Precision Standard of Frequency, Bell System Tech. J., 8, pp. 493–514: July, 1929; also Proc. I. R. E., 17, pp. 1103–1122; July, 1929.

beat where the precise measurement is made. Further discussion of the frequency at which generator P is set for the measurement will be given after describing the remainder of the procedure.

The 10 kc generator G is controlled by the primary standard which supplies current at 10 kc. Generator G is of the Hartley type having a grid resistor across which the control voltage is impressed. It remains in control over a considerable capacity change. Harmonics of the 10 kc generator G have been used in measurements as high as the 290th, but, generally speaking, harmonics below half this order are usually used.

The detector-amplifier, described in a previous paper,[12] picks up the beat frequency between generator P and generator G, as heard in telephones U. This beat frequency is matched with a similar frequency from the audio-frequency generator AF as heard in the telephones V, at a time when the setting of generator P gives a beat note in the telephones T matching tuning fork TF.

The characteristics of the generator AF are such that it will maintain its frequency over long periods. However, the calibration is not relied upon, and the output is sent into a mixing unit M or modulator which also receives a thousand cycles per second output from the primary standard S. The resulting beat frequency output from M is sent into the direct-reading frequency meter F, described in a previous reference,[13] which is checked against the hundred cycles per second output of the primary standard S. The frequency meter F is limited in range from 5 to about 200 cycles per second, but by use of the modulator M and the 1,000-cycle output from S, measurements in this range around the harmonics of 1,000 cycles per second can be made.

If it is desired to measure a frequency of approximately 20,085 kc, for example, with generator P set at such a frequency, the detector-amplifier A could hardly be expected to pick up the 2,008th harmonic of generator G. If it did, there would be an audio-frequency note of 5,000 cycles per second, which can not be measured with this equipment. Harmonics of the generator P, however, will be picked up by the radio receiver R, so that if P is set at 1/40 of [illegible] or 502 kc, the beat notes work very nicely throughout the system. In other words, when generator P is off of 1/40 the frequency of R to match tuning fork TF, the telephones U connected to A produce a note against a harmonic of the standard 10 kc generator G which can readily be matched with the note in telephones V and checked up with the frequency meter F, coming within the range of $2{,}000 \pm 200$ cycles per second. Tuning forks of several frequencies have been used to obtain check values agreeing to the order of 1 part in 10^6.

For check measurements at 5,021 kc, generator P is set in a similar manner. If the same tuning fork is used, a slightly different beat frequency is produced from that at 20,085 kc. In order to make measurements with the above apparatus at a given frequency, the harmonics and beat notes employed must bear certain relations to each other, as are stated below.

[12] See footnote 8, p. 648.

[13] See footnote 10, p. 648.

X=frequency to be measured, which is approximately known from frequency assignment.
H=frequency to which generator P is adjusted.
A=audio-frequency note produced after generator P is precisely adjusted in certain relationship to frequency X.

A should have one of the values previously mentioned; that is, 5 to 200, $1{,}000 \pm 200$, $2{,}000 \pm 200$, etc., cycles per second.

H must have a value such that—

(1) A is satisfied.
(2) Beat note between generator P and 10 kc generator G comes in the range preferably from 100 to 2,500 cycles per second.
(3) Beat note between harmonic of H and frequency X should come between 400 and 1,500 cycles per second in order to be easily matched.
(4) The frequency setting to be preferably under 1,000 kc. (Measurements have been made at three times this frequency.)

While the above conditions may seem to be quite formidable, in practice several solutions may be possible. Several measurements are possible by varying (3), using tuning forks of different frequencies. Data taken on the piezo-controlled transmitting set at NKF upon frequencies of approximately 5,021 kc and 20,085 kc gave practically the same results by the above method, although five different conditions as to beat note produced were used. It was of interest to find that measurements made at the Naval Research Laboratory by an entirely different method and in terms of a different standard, agreed with our results within about 2 parts in 10^6.

A consideration of the possibilities of error in the measurements may be of interest. Consider the measurement of 20,085.000 kc. The radio receiver, when properly set, will not introduce an error. If the radio-frequency generator was set at 1/40 the frequency to which the radio receiver was adjusted, it would be set at 502.125 kc. As it can not be set accurately here, the 40th harmonic of the generator is made to produce a 1,000 cycle difference frequency with the incoming signal. If the generator is set low, its frequency will be $502.125 - \frac{1{,}000}{40} = 502.100$ kc. If the 1,000-cycle beat note is held to 1 cycle per second, the generator is set to 1/40 cycle per second, or to $502.100 \text{ kc} \pm 0.025$ cycles. It is quite difficult, if not impossible, to hold the generator to such precision. If the generator is held so that there is a beat of 1 cycle per second, which is not impossible, the error in setting will be 1 part in 2×10^7. The error in matching the note between the standard and the generator, with the audio-frequency generator, is of considerable importance, because instead of affecting the result by 1/40, it affects it directly. The error in this matching is multiplied by 40 with the frequencies considered. However, it is possible to make the matching quite accurately, providing the radio-frequency generator holds, or the matching is carefully made when the 1,000-cycle beat note is correct. Changing the setting of a variable air condenser either side of zero beat and taking the mean setting gives a precise adjustment. The setting

of the radio-frequency generator affects the ease of this matching by a factor of 50 in this case, because the note which is matched with the audio-frequency generator is produced by the fundamental frequency (500 kc) of the generator beating with the 50th harmonic of the 10 kc generator. A change of the generator frequency of 1/40 cycle, which represents a change of 1 part in 2×10^7 with respect to the measured frequency, here produces a change of approximately 1 part in 10^5. If referred to the measured frequency this would represent a change of 0.2 kc, which is about five times the difference obtained in measured values for a given day. The factor 50, therefore, does not enter into the calculated error so much, but has more to do with the difficulties of making the measurement.

The audio-frequency generator output is then determined in terms of the direct-reading frequency meter. Errors which may be inherent in this device are likewise multiplied by 40 in arriving at the final result.

In the absence of more data the following estimates of errors in measurement may be listed. The total value thus obtained is of the same order as the departure from the mean values of frequency actually measured.

	Parts in million
Estimated error in adjusting generator to receiver	±0.5
Estimated error in adjusting audio-frequency generator to generator note	±8
Estimated error in measuring audio-generator note	±4
Total	±12.5

As the sign of the errors may be either positive or negative, some of them tend to cancel others.

The high precision and accuracy of the measurements of station frequencies by the above method arises from the use of harmonics and beat notes plus an acquired skill in the precision of setting the various parts of the equipment. The use of several tuning forks in making the settings verifies the results obtained, and in spite of a large multiplying factor, as previously stated, which applies to the errors present, the results usually agree to about 2 parts in 10^6.

Measurements on lower frequencies, such as in the broadcasting band, can be made very precisely in the above manner, and have the advantage of a small multiplying factor.

WASHINGTON, March 25, 1930.

WIND PRESSURE ON CIRCULAR CYLINDERS AND CHIMNEYS

By Hugh L. Dryden and George C. Hill

ABSTRACT

In this paper a summary is given of the published model experiments on the wind pressure on cylinders and of some previously unpublished experiments made at the National Bureau of Standards on models, on a large cylinder in natural winds, and on the power plant chimney in natural winds. This information is collected and analyzed for the purpose of estimating the wind pressure on chimneys and other cylindrical structures at known wind speeds.

The new experiments are in large measure determinations of the local distribution of pressure over the entire surface of the cylinder in the model experiments, and over a suitably chosen section in the experiments in natural winds. In addition, the overturning moment on a 10 by 30 foot cylinder in the natural wind was directly measured.

The general conclusions are as follows:

1. The wind pressure on a chimney is a function of the ratio of the height of the chimney to its diameter and possibly of the roughness of the surface.
2. Model experiments can not be directly utilized because of a large scale effect.
3. A wind pressure corresponding to 20 lbs./ft.^{2} of projected area at a wind speed of 100 miles per hour is a safe value to use in designing chimneys of which the exposed height does not exceed ten times the diameter.
4. The pressure may reach large values locally and this may require consideration in the design of thin-walled stacks of large diameter.

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I. INTRODUCTION

In Scientific Paper No. 523 of the National Bureau of Standards we have given a general discussion of the wind-pressure problem and of the results of some model experiments on the distribution of pressure over a tall building in a uniform and steady airstream. The experi-

ments described in the present paper were undertaken for the purpo of obtaining information as to the distribution of wind pressure o chimneys and other structures of substantially cylindrical form.

Because of its great complexity, we have suggested that the wi pressure problem be subdivided into several parts, namely, (1) t determination of the wind pressure in a uniform and steady wi (2) the determination of the frequency of occurrence of winds specified mean speeds as given by the Weather Bureau records, (3) t determination of the maximum gust speeds in winds of specified me speeds, and (4) the determination of the stresses produced in t several structural members by specified loadings. The division the problem into wind loads and wind stresses is well recognized, b the separation of the commonly adopted wind loads into the seve components is not often made. Too often a figure of 20, 25, or lbs./ft.^{2} is first adopted and then some method of computation found which will result in the value of the pressure originally adopte and thus in a measure justify its adoption. The loads are often sa to correspond to a speed of 100 miles per hour, a figure which seem to be regarded as a limiting value irrespective of exposure.

The problem of choosing a wind speed to be used for design pu poses is essentially a problem of probability, and unfortunately the are not sufficient data available to make an exact mathematic study possible. The period of observation for which records are ava able is not sufficiently extensive to give reliable information rega ing the frequency of very high winds. The only records availab in sufficient quantity to be useful are those of the Weather Bure on the mean speeds over 5-minute periods. In many of the record especially for stations in cities, the exposure and elevation of t anemometer have been occasionally changed, and the records are n comparable for the entire period of years. If we examine the record for a period of years at some station for which the elevation was n changed (for example, for Washington, D. C., for the years 191 1927), we find relations somewhat as follows.[1] The mean spe exceeds 40 miles per hour about 1 day in 85, 45 miles per hour abo 1 day in 195, 50 miles per hour about 1 day in 850, and 55 miles p hour about 1 day in 1,950. The maximum observed over a period 58 years was 68 miles per hour, so that the mean speed exceeds 7 miles per hour, say 1 day in 25,000. The engineer must decide ho much risk should be covered in the form of wind-storm insuran rather than in increased strength of construction. If, for examp he decides to design for a load that will occur on the average on once in 20 years, the above figures indicate a mean speed over fi minutes in the neighborhood of 60 miles per hour.

The figures published by the Weather Bureau are the uncorrecte readings of a Robinson type cup anemometer. Before January 1928, a 4-cup driving unit was used, but on that date a change w made to a 3-cup unit because of the large errors of the older instru ment at high speeds. The speeds indicated by the old and the ne instruments at various true speeds are given to the nearest mile p hour in Table 1. From the table it is seen that the indicated spee of 60 miles per hour by the old standard corresponds to a true speed o 47 miles per hour.

[1] These figures are illustrative only. While approximately correct, they are not intended for use design. The data are taken from the annual reports of the Chief of the Weather Bureau.

TABLE 1.—*Indicated wind speeds by Robinson cup anemometers* [1]

True speed (miles per hour)	Indicated speed, old 4-cup standard	Indicated speed, new 3-cup standard	True speed (miles per hour)	Indicated speed, old 4-cup standard	Indicated speed, new 3-cup standard
5	5	5	60	78	63
10	11	10	65	85	68
15	17	15	70	91	73
20	23	20	75	98	79
25	30	25	80	105	84
30	37	31	85	112	89
35	44	36	90	118	95
40	50	41	95	125	100
45	57	47	100	132	105
50	64	52	105	138	111
55	71	57	110	145	116

[1] Before Jan. 1, 1928, the U. S. Weather Bureau used the 4-cup instrument; after that date, the 3-cup.

Little information is available as to the relation of the speeds of sts to the mean speed over five minutes. It is commonly assumed t the maximum gust speeds will be about 50 per cent greater than e mean over five minutes, and the few observations which we have de indicate that this is true at speeds below 40 miles per hour d at elevations less than 150 feet above the ground. There is a neral belief that in high winds the speed is more uniform, and it known that the gustiness decreases with increasing elevation. the engineer assumes that that ratio of the gust speed to the mean ed over five minutes is 1.5, the actual design speed finally arrived in the above example is 71 miles per hour. We repeat that the ures given are only illustrative of a logical method of procedure d are not intended as design recommendations. Larger values uld be found for more exposed locations, such as the New York and icago stations.

The work of the Bureau of Standards has been largely confined a determination of the pressures encountered in a steady and uni- rm wind, especially as affected by the shape of the body. The sults of our experiments are often interpreted in terms of wind adings at a convenient wind speed, such as 100 miles per hour, and is seems desirable for the benefit of those to whom the concept of rce coefficient is new and unfamiliar. We wish to emphasize, owever, that our work is concerned with but one element of the roblem, and that we do not recommend the indiscriminate use of 100 iles per hour as the wind speed the structure must be designed to ithstand. Neither are we in a position to make positive recom- endations as to design loads. These should logically depend on the eographical location of the structure and the degree of its exposure, nd should be correlated with the working stress and factor of safety sed in the design.

I. SUMMARY OF AERODYNAMIC DATA ON CYLINDERS

Before making a summary of the published work on cylinders it is ecessary to review briefly the conventional method of presenting erodynamic data. Dimensional reasoning teaches that the pressure, , at any point of a body placed in an air stream will be given by an xpression of the form

$$p/q = f\left(\frac{VL\rho}{\mu}\right)$$

where q is the velocity pressure ($\frac{1}{2}\rho V^2$), ρ is the air density, V wind speed, μ the viscosity of air, and L a linear dimension fixing scale, taken as the diameter in the case of cylinders. The expres applies only to geometrically similar bodies, for example, to cylind of infinite length or of constant ratio of length to diameter. pressure, p, may be regarded as consisting of two parts, the st pressure,[2] p_s, which would exist in the absence of the cylinder, the pressure change, $p-p_s$, caused by the presence of the cylind In a natural wind p_s is the atmospheric pressure. $p-p_s$ is the qu tity usually measured, corresponding to the common practice using "gauge" pressure in dealing with pressures in steam boil compressed air tanks, etc., rather than absolute pressure. The pr sure difference could be measured in any convenient units, but th are advantages in using the velocity pressure, $q=\frac{1}{2}\rho V^2$, as the u

In the first place $\frac{p-p_s}{q}$ is in many cases[3] independent of the wi speed and the size of model, so that from a single value of it for a given shape of body the pressure at the corresponding point on similar body of any size at any wind speed can be readily comput with the aid of a table of velocity pressures. In many other ca the variation of $\frac{p-p_s}{q}$ with the Reynolds number $\frac{VL\rho}{\mu}$ is small. T ratio is a pure number independent of the units used so long as t pressures are all measured in the same units.

TABLE 2.—*Velocity pressures at several wind speeds*

True wind speed (miles per hour)	Velocity pressure (lbs./ft.²)	True wind speed (miles per hour)	Velocity pressure (lbs./ft.²)
5	0.064	65	10.81
10	.256	70	12.53
15	.575	75	14.39
20	1.023	80	16.37
25	1.600	85	18.48
30	2.302	90	20.72
35	3.133	95	23.08
40	4.092	100	25.58
45	5.179	105	28.20
50	6.394	110	30.95
55	7.737	115	33.83
60	9.208	120	36.83

NOTE.—Velocity pressure in lbs./ft.^{2}=0.001189 $(V\times\frac{22}{15})^2$ where V is the true speed in miles per hour, a the density is that at 15° C.

The engineer is in most cases more directly concerned with th resulting forces than with the pressures themselves and their distr bution. The force on any element, dA, is equal to pdA and acts the direction of the normal to the surface.[4] If θ is the angle ma by the surface element, s, with the wind direction, the component force in that direction, F_s, is given by $\int\int pdA$, sin θ. Since p_s

[2] The term static pressure is used to indicate the pressure which would be measured by a pressure gau moving with the air and, therefore, "static" with respect to the air. In actual practice the measureme is made by means of holes in the side of a closed tube, the axis of which is parallel to the wind direct The form of the tube is such that the air flows smoothly past the holes.

[3] B. S. Sci. Paper No. 523, Bull. **20**, p. 697.

[4] Excluding frictional effects, which are of importance only in special cases.

stant and for closed surfaces $\int\int dA \sin\theta = 0$, the force component closed surfaces is also given by $\int\int (p - p_s) dA \sin\theta$. Dividing q, we have $\frac{F_s}{q} = \int\int \frac{p - p_s}{q} dA \sin\theta$. It is found convenient to ide this expression by the area of projection, A_p, of the body on a ne normal to the direction, s. The quotient $F_s/A_p q$ is called the ce coefficient.[5] It is the average force per unit projected area ided by the velocity pressure; that is, the ratio of the average ssure on the total projected area to the velocity pressure. The ce in any particular case is obtained by multiplying the force efficient by the projected area and by the velocity pressure.

In the case of a chimney or similar structure, the distribution of d along the length is sometimes of interest. In this case we com-te the force per unit length $\frac{dF_s}{dl} = \int p\, ds \sin\theta$, where $ds\, dl$ is the area ement, dA. Again it is convenient to divide $\frac{dF_s}{dl}$ by the width of the ction (the diameter in the case of a cylinder) and by the velocity ssure q so as to obtain a coefficient applicable to the particular ction, giving the average force per unit area per unit velocity ssure. To distinguish this coefficient from the force coefficient plicable to the whole cylinder, we call it the force coefficient for a nsverse section. In all cases the force is obtained readily by ltiplying the coefficient by an area and by the velocity pressure.

In the case of bodies with sharp edges, such as flat plates, models of ildings, etc., the coefficients defined in this manner are so nearly nstant that departures obtained in a few experiments are believed be due to secondary causes, such as the limited size of air stream ed, or the effects of supports. For cylinders and spheres, on the her hand, the coefficients are constant only over a limited range of lues of $VL\rho/\mu$. This lack of constancy is called scale effect, since e coefficient varies with the size of the model. Spheres have ceived the more complete study. It was discovered by Costanzi [6] r spheres in water and by Eiffel [7] for spheres in air that the force efficient for large spheres decreases rapidly at a certain critical eed. Lord Rayleigh [8] pointed out that the critical speed varied with e diameter of the sphere in such a manner that the Reynolds mber was constant. Actually, the critical speed is not a definite ed speed but rather a range of speeds, corresponding to a certain gion of Reynolds number in which the force coefficient decreases pidly; this is followed by a region in which the force coefficient is rly constant. In further experiments it was found that the rapid crease took place at different values of the Reynolds number in fferent wind tunnels and at different values in the same wind tunnel ith different types of spindles or supports.[9] The degree of turbu-nce of the air stream was found to be a very important factor.

Additional information was given by Wieselsberger [10] who showed, y introducing smoke in the air stream, that the turbulent wake was

[5] The terms, resistance coefficient, drag coefficient, shape coefficient, are also used.
[6] Alcune esperienze di idrodinamica, 2, No. 4; Rome 1912.
[7] Comptes Rendus, 155, p. 1597; Dec. 30, 1912.
[8] Comptes Rendus, 156, p. 109; Jan. 13, 1913.
[9] See for example the following summaries: Technical Report No. 185, National Advisory Committee for Aeronautics; Reports and Memoranda No. 190, Brit. Adv. Comm. Aero.; Annual Report, Brit. Adv. Comm. Aero., 7, p. 19; 1915–16.
[10] Zeitschrift fur Flugtechnik und Motorluftschiffahrt, 5, p. 140; 1914.

much smaller above the critical region than below it, and that smo flow around the sphere continued well past the major section. It w also found that the flow, and hence the force, was most sensitive disturbances in the "boundary layer" or layer of air passing v close to the sphere, and it was suggested that the change in the gene flow at large Reynolds numbers resulted from the flow in this t layer passing from the smooth viscous flow régime to the turbul régime, analogous to the change in the type of flow in pipes, f described by Reynolds.[11]

In short, the change in the force coefficient was found associat with a change in the position of the line at which the smooth flow l the surface of the sphere. It may be expected then that no scale-effe would be found in the case of bodies with sharp edges which definite fix this line, and that spherical and cylindrical forms would be t most sensitive. This is, in fact, the case, as is shown by measuremen on ellipsoids by Wieselsberger.[12] The position of the line of sepa tion in the case of an isolated sphere would be determined solely b the loss of energy in the flow near the surface. This loss depends to large extent on the turbulence of the air flow, and that is changed b the presence of the rods or wires needed for supporting the sphere.

Similar phenomena are observed with cylinders. Experiment evidence of the existence of a critical region for cylinders was fi published by Taylor.[13] In some measurements on a 6-inch cylind in a 4-foot wind tunnel he found a large variation of the pressure di tribution with wind speed, the nature of which will be discussed late Force measurements in this region were made subsequently b Eiffel [14] and by Wieselsberger.[15]

The influence of the flow in the boundary layer and the effect turbulence were shown experimentally by one of the authors a R. H. Heald.[16]

The force coefficients for cylinders depend on the Reynolds numbe the ratio of length to diameter, the turbulence of the air stream, an perhaps, on the roughness of the surface. The effects of turbulen are marked only in the region of Reynolds numbers between 100,0 and 500,000. Figure 1 gives the results of Relf [17] and Wieselsberger for cylinders of infinite length (actually of finite length, but und conditions approximating two dimensional flow) over a wide range Reynolds number. These values may be used in computing t wind pressure on long wires, masts, flagpoles, and similar structure For this purpose the kinematic viscosity (the ratio of the viscosity, to the density, ρ) may be assumed to be 0.000161 ft.^{2}/sec. and t Reynolds number taken equal to the product of wind speed in mil per hour by diameter of cylinder in feet by the constant 9,100.

Wieselsberger gives some information as to the variation of for coefficient with length-diameter ratio at a Reynolds number of 80,00 The values are given in Table 3.

[11] Phil. Trans. Roy. Soc. (London), **174**, Pt. III, p. 935; 1883. For a further development of these ide see Technical Report 342 of the National Advisory Committee for Aeronautics.
[12] Zeitschrift fur Flugtechnik und Motorluftschiffahrt, **5**, p. 140; 1914.
[13] Reports and Memoranda, No. 191, Brit. Adv. Comm. Aero. Annual Report, **7**, p. 30; 1915-16.
[14] Travaux Laboratoire Aerodynamique Eiffel (E. Chiron, Paris), p. 60, 1915–1918.
[15] Ergebnisse der Aerodynamischen Versuchsanstalt, Göttingen, 1923 (R. Oldenbourg), **2**, p. 23.
[16] Technical Report No. 231, National Advisory Committee for Aeronautics.
[17] Reports and Memoranda No. 102, Brit. Adv. Comm. Aero. Annual Report, **5**, p. 47; 1913–14.
[18] Physikalische Zeitschrift, **23**, p. 219; 1922.

TABLE 3.—*Effect of length-diameter ratio on force coefficients of cylinders at a Reynolds number of 80,000*

Length-diameter ratio	1	2	3	5	10	20	40	∞
Force coefficient	0.63	0.69	0.75	0.74	0.83	0.92	1.00	1.20

The cylinders of length-diameter ratios 5 and ∞ were carried through a wide range of Reynolds numbers and a comparison of the results seems to indicate a smaller effect of length-diameter ratio above the critical region.

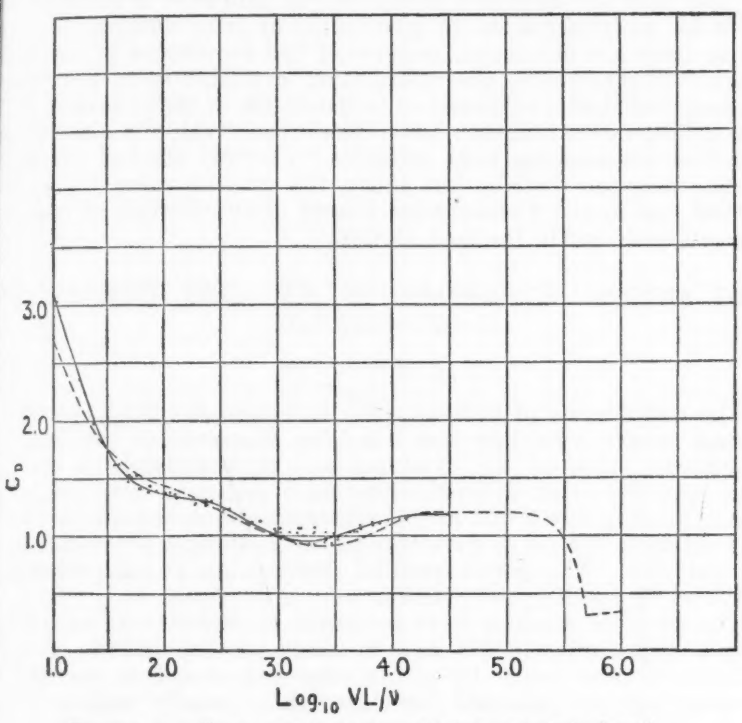

FIGURE 1.—*Force coeffcients for cylinders of infinite length*

C_D=force coefficient.
V=wind speed (ft./sec.).
L=diameter (ft.).
ν=kinematic viscosity (ft.²/sec.).
=0.000161 for air.
———— Relf.
---------- Wieselsberger.

In addition to measurements of the total force on the whole cylinder, a number of measurements of the distribution of pressure around the cylinder have been published. These experiments will be summarized and discussed a little later in connection with the results described in this paper.

Several important investigations relating to the flow around cylinders have also been published. For Reynolds numbers between 100 and the critical value, the flow is known to vary with the time, eddies breaking off periodically. The frequency of the eddy formation has

been studied by Karman[19] and Relf.[20] For approximate computations at Reynolds numbers below the critical value the product of frequency (cycles per second) by diameter of the cylinder (in feet) may be taken as 0.29 times the wind speed in miles per hour. At the critical Reynolds number the frequency increases more rapidly with the speed, and finally the flow loses its periodic character; it continues to vary with time, but in an erratic manner. It is obvious that conditions of resonance in wires or flagpoles in high winds are to be avoided, and it seems probable that the erratic fluctuation of the flow may set up severe oscillations in chimneys of small stiffness.

Model experiments fail to give values of force coefficients applicable to full-scale chimneys, because of the occurrence of the critical region. Furthermore, the information available as to the effect of the length-diameter ratio and as to the details of the pressure distribution at Reynolds numbers above the critical value is quite limited. Our first experiments were intended to supply further information on the pressure distribution above the critical value. They were carried out in the 10-foot wind tunnel of the Bureau of Standards and are described in the next section.

III. MODEL EXPERIMENTS AT THE BUREAU OF STANDARDS

1. APPARATUS

The distribution of pressure over two circular cylinders with axes normal to the wind direction has been measured at the Bureau of Standards. One of the cylinders was approximately 8 inches in diameter, the other approximately 12.6 inches in diameter. Each was approximately 5 feet long. Observations were made at 12 pressure stations, spaced as shown in Figure 2, along a generating line of the cylinder. The circumferential distribution at each station was obtained by rotating the cylinder.

The pressure stations were prepared as follows: At each station a hole approximately 0.2 inch in diameter was drilled. A hollow cylindrical plug about 1¼ inches long and closed at one end was sweated into the hole and the closed end carefully worked down so as to make it flush with the outer surface of the cylinder. After polishing, a small hole approximately 0.040 inch in diameter was drilled along the axis of the plug into the tubular portion. By means of rubber tubing, connection through the interior of the cylinder could then be made from each station to the pressure gauge.

The same mounting was used for the 8-inch cylinder as for the prism described in Scientific Paper No. 523. The cylinder was rigidly attached to a round steel plate, 12 inches in diameter and ¼ inch in thickness, bearing graduations at 5° intervals along its circumference. The cylinder and plate could be rotated on a bearing fastened to a plate 14 inches square and ⅜ inch thick, which carried an index mark. The cylinder proper was a piece of drawn brass tubing, 4 feet 11 inches long, and was accurately a circular cylinder within ±0.01 inch. The departures were greatest near one end (the upper), and

[19] Physikalische Zeitschrift, **13**, p. 49; 1912.
[20] Phil. Mag. (6th series), **42**, p. 173; 1921. Reports and Memoranda of the British Aeronautical Research Committee, Nos. 825, 917, and 986.

ver the greater part of the length were less than 0.015 inch. The op of the cylinder was closed by a plate 3/16 inch thick. The total ngth from the bottom of the ounting to the top of the top late was 5 feet 7/16 inch, of which inch was taken up in the mount- g plates.

The 12.6-inch tubing was more ccurately of the form of a circular ylinder. The average diameter as 12.62 inches with departures ss than ±0.01 inch. A somewhat eavier mounting was required; the pper plate to which the cylinder as attached was 15 inches in dia- eter and ½ inch thick, and the ower plate carrying the bearing as 17¾ inches in diameter and 1⅜ nches thick. The cylinder proper as exactly 5 feet long and the top late was ⅛ inch thick. The total ength was 5 feet 2 inches, of which ⅞ inches was taken up in the ounting plates.

The wind stream was supplied y the 10-foot wind tunnel which s described in Scientific Paper o. 523. The method of measur- ng wind speed and the pressure auge used for measuring pressures t the station on the cylinders were escribed in the same paper. In he present tests speeds up to about 6 miles per hour were obtained.

The effect of the ground on which he chimney stands was simulated y a platform placed under the odel. The platform extended ompletely across the tunnel and as 2 feet above the tunnel floor t the center. Its length in the irection of the wind was 5 feet and ts upstream edge was beveled so as o reduce the disturbance produced y it. The wind speed was nearly niform to within a few inches of he platform.

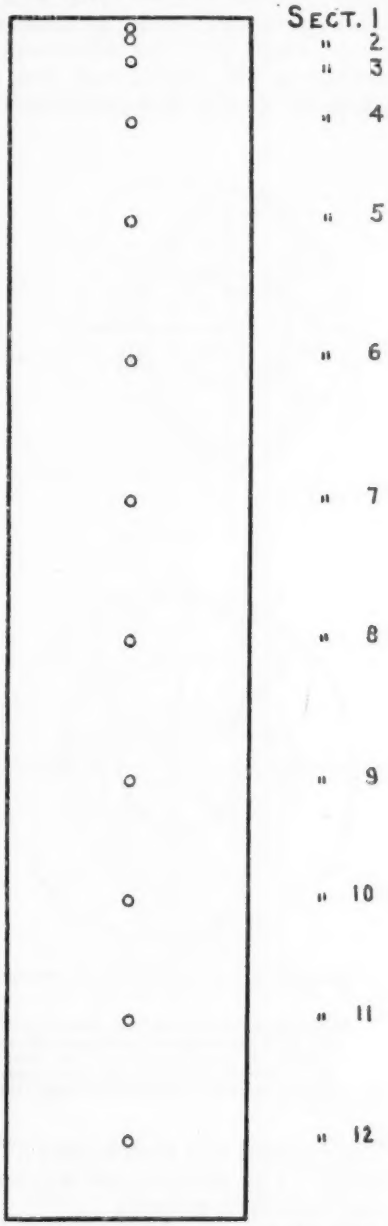

FIGURE 2.—*Location of pressure stations on cylinders in wind-tunnel tests*

2. GENERAL PROCEDURE

The procedure for making the observations was as follows: The 12 pressure stations were connected to 12 tubes of a multiple tube manometer, the reservoir of the manometer being connected to a

small hole in a static plate located 7¾ feet upstream from the model on some occasions, to a small hole in the downstream quadrant of a short cylinder placed with axis normal to the wind.[21] When the wind speed was steady, an observer read the 12 tubes of the multiple gauge, which gave the differences in pressure between the holes at the surface of the model and the reference pressure. Readings were taken for speeds of approximately 40, 60, 80, and 97 feet per second.

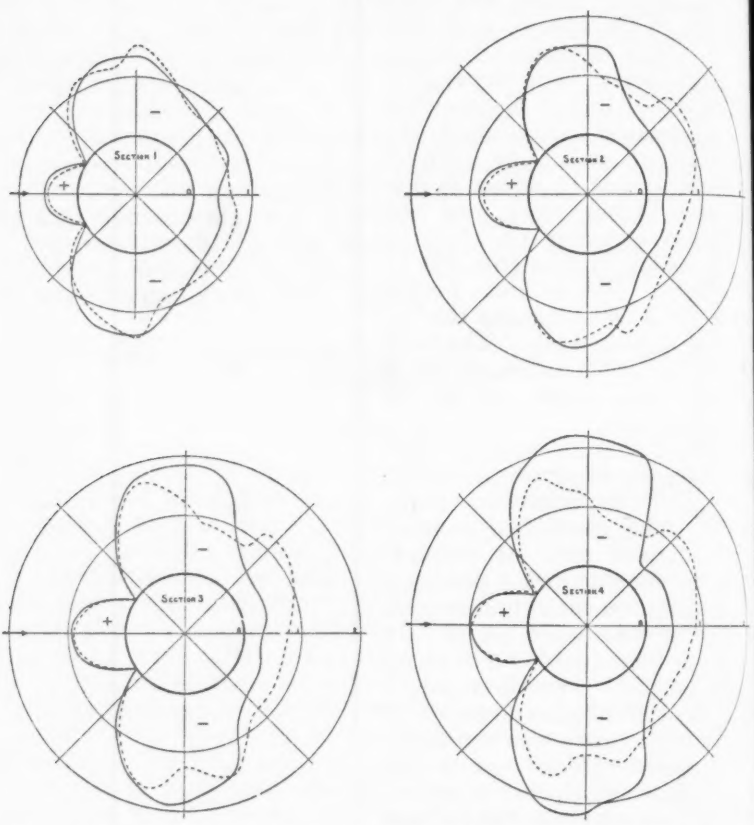

FIGURE 3.—*Distribution of pressure on 8-inch cylinder at sections 1, 2, 3, and 4*

Radial distances from the base circle are proportional to the ratio to the velocity pressure of the difference in pressure between the station and the static pressure. In the region marked +, the pressure on the cylinder exceeds the static pressure, while in the region marked −, the pressure on the cylinder is less than the static pressure. The wind direction is shown by the arrow. The broken line is for a speed of 40 ft./sec., the solid line for 80 ft./sec. See Figure 2 for location of sections.

The cylinder was then turned 5° and a similar group of measurements made. The process was continued until the full angular range of 360° had been covered.

The results finally desired are the changes in pressure produced by the presence of the cylinder. It was necessary, therefore, to measure the difference in pressure between the reference pressure and the

[21] This was done in order to keep the differential pressure within the range of the multiple manometer

tic pressure in the tunnel at the place previously occupied by the linder and to add this value with proper sign to the observed essure. It was also necessary to correct for the difference in wind eed between the place where the reference Pitot-static tube was cated and the position of the model.

All results in this paper have been expressed as ratios of the several uantities to the velocity pressure, a plus sign being used to denote

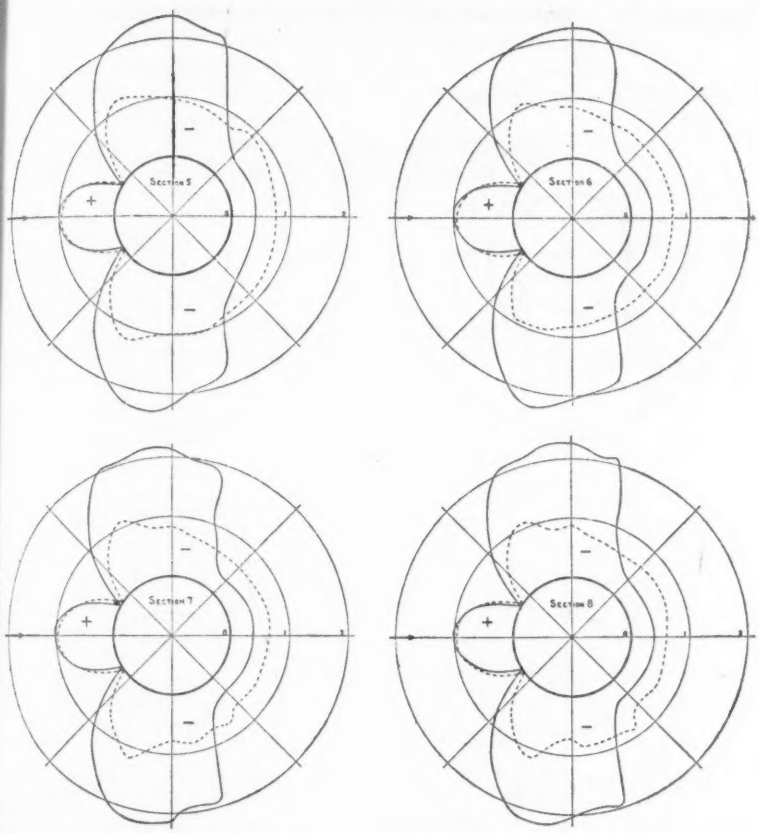

FIGURE 4.—*Distribution of pressure on 8-inch cylinder at sections 5, 6, 7, and 8*

For explanation, see legend of Figure 3

n increase in pressure above the static pressure and a minus sign to denote a decrease.

The average pressure acting at each section on the area of projection f the cylinder on a plane normal to the wind and the average pressure cting on the entire cross-sectional area were each computed by umerical integration. These results give the load distribution along he length and the total force on the cylinder. Resultant forces at ight angles to the wind direction are small and would be exactly zero if he pressure distribution were exactly symmetrical.

3. RESULTS

The pressure distribution for the four air speeds are given in part the polar diagrams of Figures 3 to 8, inclusive. The distributions average force per unit projected area along the length are given Figures 9 and 10 and the average force per unit projected area for t whole cylinder in Figure 11. The quantities plotted are absolu coefficients, the values of which do not depend on the system units, provided a self-consistent system is used throughout.

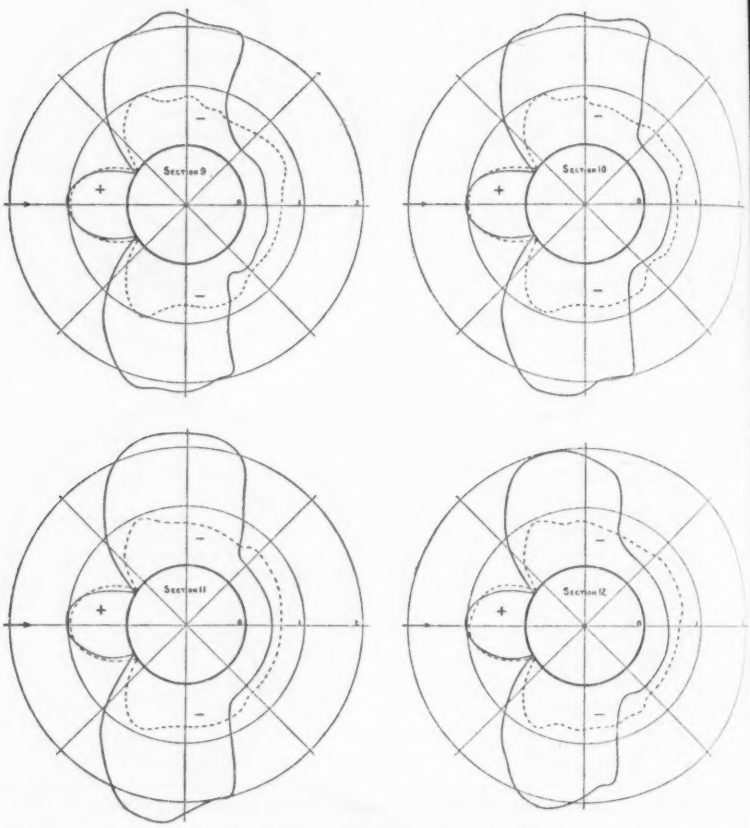

FIGURE 5.—*Distribution of pressure on 8-inch cylinder at sections 9, 10, 11 and 12*

For explanation, see Figure 3

The coefficients are defined as follows:

$$C'_D \text{ at any section} = \frac{1}{w}\int \frac{p-p_s}{q} \sin\theta \, ds$$

$$C_D \text{ for the whole cylinder} = \frac{1}{wl}\int \frac{p-p_s}{q} \sin\theta \, ds \, dl = \frac{\text{total force}}{wlq}$$

where w = width of projection on a plane normal to the wind = diameter of cylinder.
l = length of the cylinder.
$dsdl$ = element of area on the surface of the cylinder. (Note that $ds \sin \theta = dw$.)
θ = angle between the surface element of the cylinder at any point and the wind direction; that is, the complement of the zonal angle, 90°—the zonal angle, of the station measured from the upstream generating line.
q = the velocity pressure (Table 2).
$p - p_s$ = the difference between the pressure at any station and the static pressure.
C'_D = force coefficient for transverse section.
C_D = force coefficient for whole cylinder.

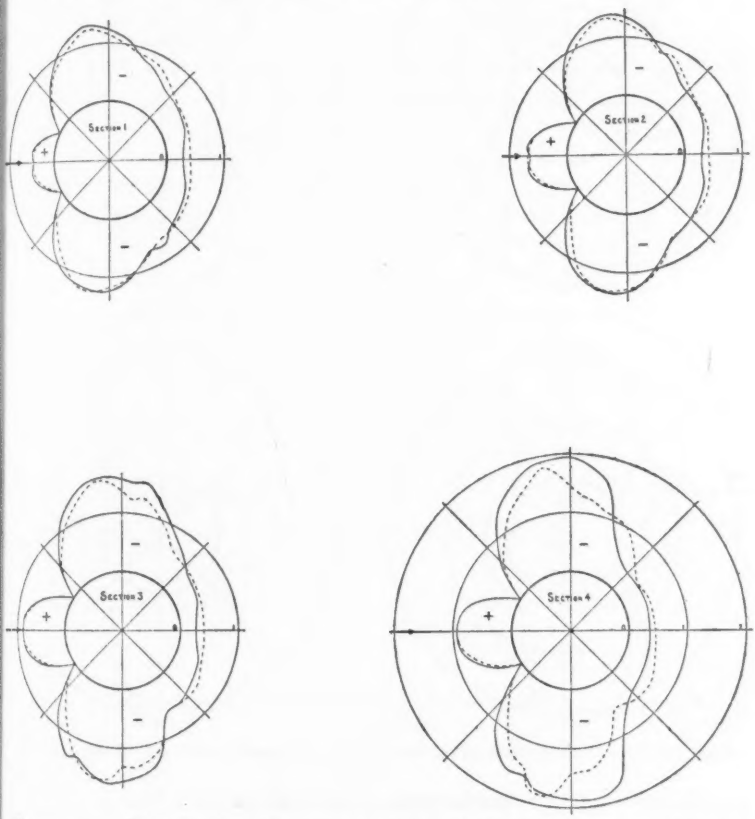

FIGURE 6.—*Distribution of pressure on 12.6-inch cylinder at sections 1, 2, 3, and 4*
For explanation, see legend of Figure 3

The force per unit length at any section is obtained by multiplying the value of C'_D at that section by the width of the section and the velocity pressure. The total force is obtained by multiplying the value of C_D for the whole cylinder by the area of projection on a plane normal to the wind, that is wl, and the velocity pressure.

It will be seen that all of the coefficients vary greatly with t
wind speed, differing in this respect from those for the prism mo
of Scientific Paper No. 523. Dimensional reasoning teaches, as in
cated before, that provided the objects are geometrically similar t
pressure should be a function solely of the Reynolds number, $VL\rho/\mu$,
V being the wind speed, L a linear dimension fixing the scale and tak
equal to the diameter, ρ the density and μ the viscosity of the a
The two cylinders are not geometrically similar to each other; nev
theless at high Reynolds numbers the results for the two agree fai
well. (See fig. 11.)

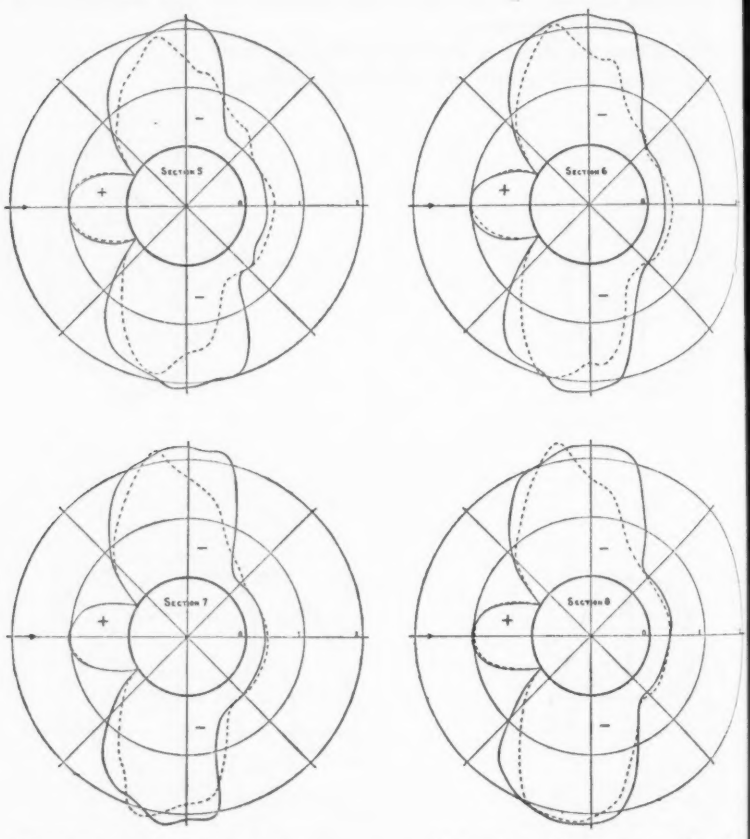

FIGURE 7.—*Distribution of pressure on 12.6-inch cylinder at sections 5, 6, and 8*

For explanation, see legend of Figure 3

4. DISCUSSION AND COMPARISON WITH OTHER PUBLISHED DATA

All of the speeds used for the 8-inch cylinder are equal to
greater than the critical value. Because of this fact the computati
of average pressures is subject to a small error. For, owing
changes in the barometric pressure and the temperature of the a
the kinematic viscosity and, hence, the Reynolds number for a giv
air speed changes from day to day. The total range in values of

ynolds number at a given speed was about 3 per cent. The effect the value of the average pressure is probably not very great.

A careful examination of the diagram shows a lack of symmetry th respect to the wind direction. By reading off the angles at ich $p-p_s$ vanishes we may estimate the nature and amount of e asymmetry. Figure 12 shows the average angle of asymmetry or gle through which the diagram for each section must be rotated to ng the points of zero pressure difference to symmetrical positions.

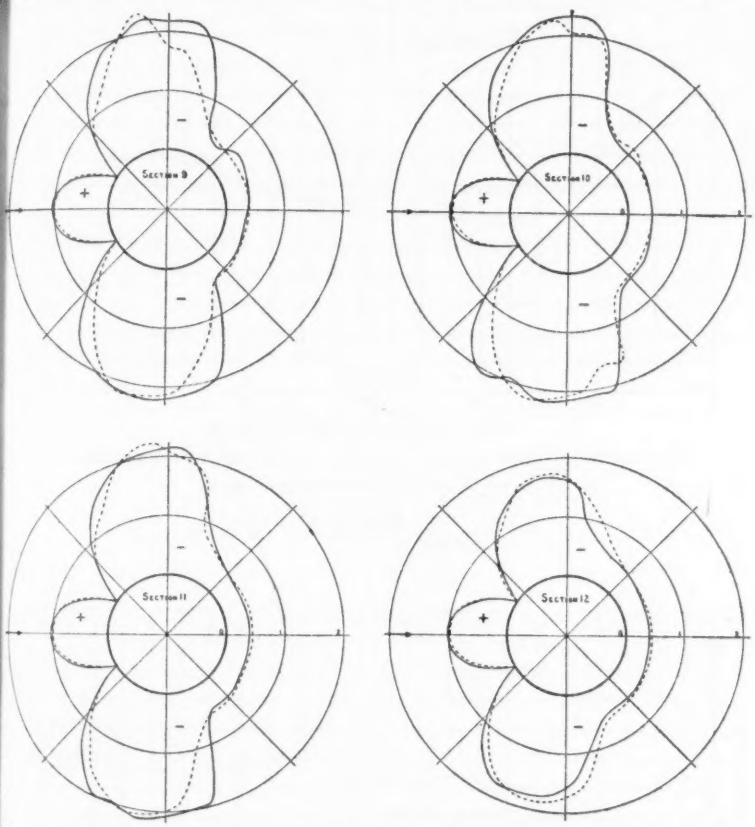

FIGURE 8.—*Distribution of pressure on 12.6-inch cylinder at sections 9, 10, 11, and 12*

For explanation, see legend of Figure 3

he figure shows a systematic and approximately linear variation of ughly ½° per foot of height corresponding to a rotation in the direcn of travel of the propeller blades. Measurements in the absence the cylinders with an instrument for measuring the direction of flow show a spin in the air stream of about one-half this amount. The projected area of the 12.6-inch cylinder was about 7 per cent the tunnel area, and that of the 8-inch cylinder about 4½ per cent the tunnel area. The only experiments available on the effect of nnel size are those of Parkin [22] and they are based on the theory

[22] J. Royal Aero. Soc., **31**, p. 1110; 1927.

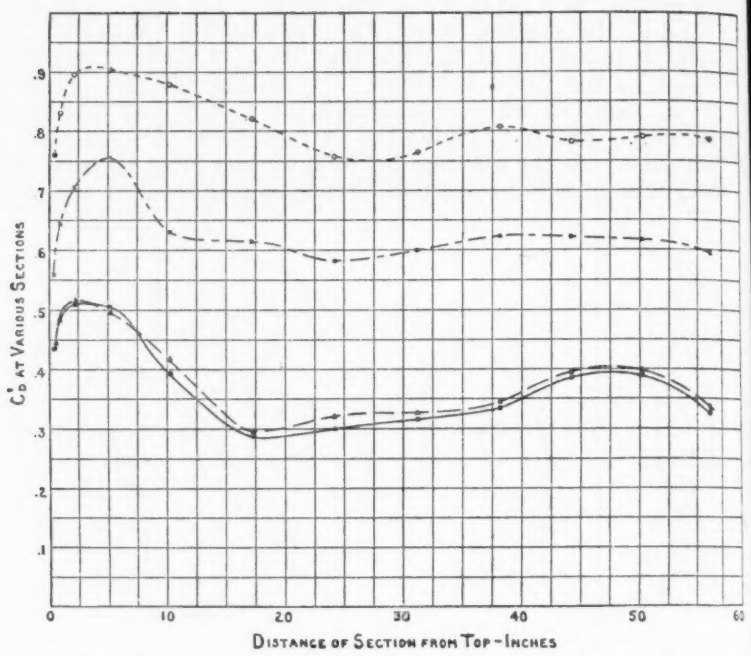

FIGURE 9.—*Distribution of pressure along the 8-inch cylinder*

C_D'=force coefficient for transverse section—
- - - - 40 ft./sec.
— ——— — ——— 60 ft./sec.
——————— 80 ft./sec.
— — — 97 ft./sec.

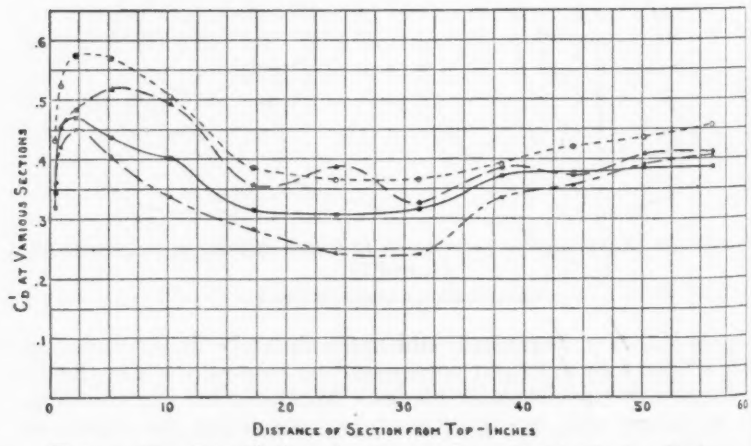

FIGURE 10.—*Distribution of pressure along the 12.6-inch cylinder*

C_D'=force coefficient for transverse section—
- - - - 40 ft./sec.
— ——— — ——— 60 ft./sec.
——————— 80 ft./sec.
— — — — — — 97 ft./sec.

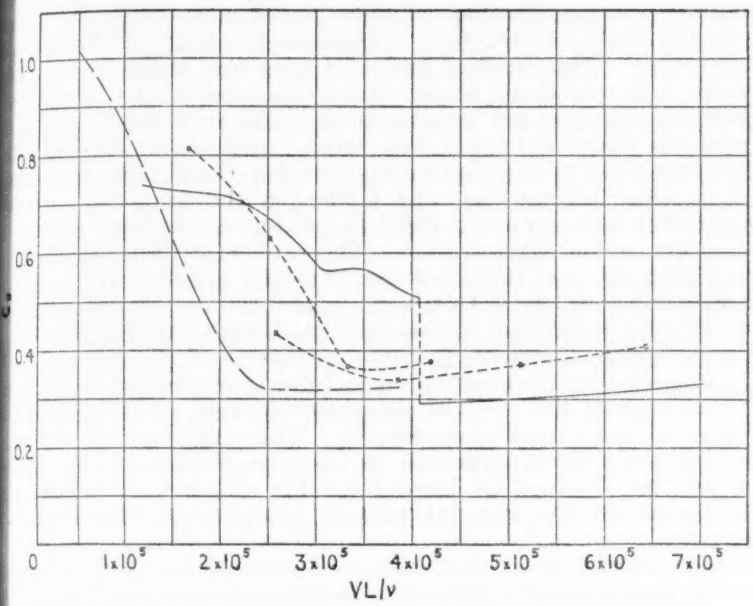

FIGURE 11.—*Force coefficients for cylinders at large Reynolds numbers*

C_D=force coefficient (for the whole cylinder).
V=wind speed (ft./sec.).
L=diameter (ft.), ν=kinematic viscosity (ft.²/sec.)=0.000161 for air.
———— ———— Eiffel.
———————— Wieselberger.
o - - - - Dryden and Hill, 8-inch cylinder.
x - - - - Dryden and Hill, 12.6-inch cylinder.

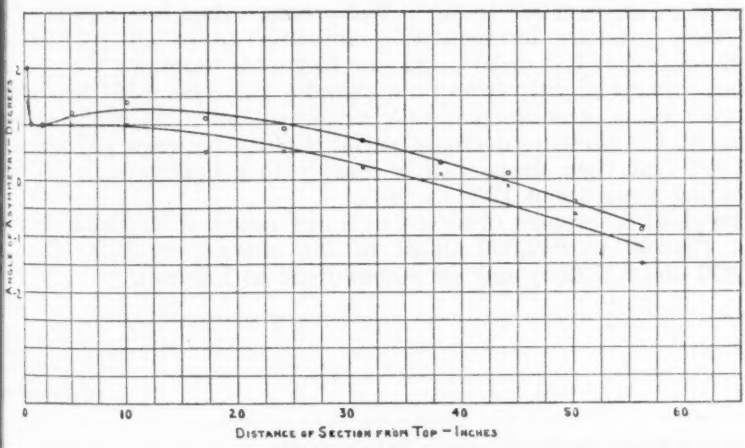

FIGURE 12.—*Angle through which the pressure diagrams for the various sections must be rotated in order to give symmetrical positions for the points of zero pressure difference*

of images. In other words, the tests actually made were on a cylin der in the presence of other cylinders placed in positions correspond ing to the images of the first cylinder in the walls of the fictitio small tunnel. The smallest projected area was about 1.8 per cen and the next was about 35 per cent of the area of the tunnel cro section, so that it is not possible to estimate very closely where th effect of the tunnel walls begins to exceed a predetermined small valu The values of the ratio which we have employed are in line with value used in other laboratories. At Göttingen the projected area wa about 11 per cent and at the Eiffel Laboratory about 9 per cent of th area of the tunnel cross section. The ratio of cylinder diameter t tunnel diameter was 0.105 for the 12.6-inch cylinder, 0.067 for th 8-inch cylinder, 0.134 at Göttingen, and 0.100 at the Eiffel Labora tory. Taylor states that a ratio of 0.125 is evidently too large.

We recognize, therefore, that the conditions of the experiment d not correspond to ideal conditions as fully as one might desire, espe cially as regards the ratio of the projected area of the cylinder t the area of the tunnel cross section. The conditions do, however represent the nearest approach to ideal conditions in this respec that can be obtained at large Reynolds numbers in atmospher wind tunnels of the sizes at present available at the Bureau Standards.

The observed type of distribution of pressure is well known fro previous measurements, differences being matters of detail as to rel tive numerical values. In every case except for sections 1 to which are in the uppermost 5 per cent of the length, the maximu pressure increase on the front is equal to the velocity pressure withi 2 per cent, hence within the experimental error. The point of max mum pressure is within 1° of the point farthest upstream and th variations within this limit which have been previously discussed a at least partly due to a slight spiral motion in the air stream. Th pressure falls off to either side and reaches the static pressure at zonal angle of from 31° to 35°. The pressure then becomes less tha the static pressure by increasing amounts up to an angle in th neighborhood of 65° to 75°. At low Reynolds numbers, the pressur decrease drops slightly from its maximum value near 70° to a nearl constant value extending from 85° or 90° to 180°. At high Reynold numbers, the pressure decrease varies slightly between 70° and 100 or 100° and then drops rather sharply to a nearly constant valu extending from about 135° to 180°.

The chief differences observed over the range of Reynolds numbe from 168,000 to 642,000 (most of the change occurring betwee 252,000 and 257,000) may be summarized as follows:

	Reynolds No.	
	168,000	642,000
1. Zonal angle at which the pressure is equal to the static pressure	35°	3
2. Maximum pressure decrease below the static pressure, expressed as a ratio to the velocity pressure	1.2	2
3. Mean pressure decrease over rear quarter of cylinder, expressed as a ratio to the velocity pressure	.7	

These changes, especially the last two, are well shown in Figures 4, and 5. The excessive development of the winglike protuberances extending across the direction of the air stream are characteristic of Reynolds numbers above the critical value.

Table 4 gives all of the published information which we have been able to find on the general characteristics of the pressure distribution around circular cylinders. As it seems probable that a cylinder spanning an open air stream does not act as a cylinder of infinite length (owing to the feeding of air into the low pressure regions at the ends), the results of Hemke (serials 15 and 16) and of Toussaint and Weisenburger (serial 17) have been considered applicable to cylinders having lengths equal to the diameter of the air stream, and those are the lengths tabulated. On the other hand, when a cylinder in a tunnel stands on a large platform, the data are applicable to a cylinder without a platform and of twice the actual length-diameter ratio. Consequently, the tabulated values of that ratio for serials 1 to 43, inclusive, are twice the actual.

TABLE 4.—*General characteristics of pressure distribution on circular cylinders*

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2	F. Eisner	Z. f. angew. Math. u. Mech., **5**, p. 486; 1925.
3	A. Fage	British Advisory Committee for Aeronautics, Annual Reports, **5**, p. 65; 1913–14.
4	A. Fage	Aeronautical Research Committee, Reports and Memo. No. 1179.
5	P. E. Hemke	National Advisory Committee for Aeronautics, Technical Note No. 250.
6	J. H. Parkin	J. Roy. Aero. Soc. (Gt. Brit.), **31**, p. 1110; 1927.
7	T. E. Stanton	Aeronautical Research Committee, Reports and Memo. No. 1210.
8	G. I. Taylor	British Advisory Committee for Aeronautics, Annual Reports, **7**, p. 30; 1915–16.
9	A. Thom	Aeronautical Research Committee, Reports and Memo. No. 1194.
10	A. Toussaint and Lt. Weisenburger	Aeronautique, **2**, p. 456, 493; 1920.
11	H. L. Dryden and G. C. Hill	Present work.

Serial No.	Dimensions of cylinders	Ratio [1] of length to diameter	Reynolds No. R	$\log_{10} R$	Angle from wind direction at which pressure equals static pressure to nearest degree	Mean decrease in pressure over rear quarter	Maximum decrease in pressure	Angular width of pressure hole	Ratio of cylinder diameter to tunnel diameter	Ratio of cylinder area to tunnel area	Reference number in bibliography	Remarks
	Inches				*Degree*	*Per cent of q*	*Per cent of q*	*Degree*				
1	0.025 by 26	∞	28	1.447	44	47	89	36	0.001	0.001	9	
2	.025 by 26	∞	70	1.845	37	53	96	36	.001	.001	9	
3	.125 by 26	∞	144	2.158	34	80	105	4	.005	.005	9	
4	.025 by 26	∞	250	2.398	33	88	117	28	.001	.001	9	
5	.125 by 26	∞	360	2.556	32	87	117	4 14	.005	.005	9	
6	.025 by 26	∞	484	2.685	33	84	104	28	.001	.001	9	Correction made for angular width of hole.
7	.125 by 26	∞	1,245	3.095	32	76	105	4 14	.005	.005	9	
8	.125 by 26	∞	2,520	3.401	34	81	110	4 14	.005	.005	9	
9	.875 by 26	∞	2,900	3.462	36	70	97	2	.032	.032	9	
10	.875 by 26	∞	8,500	3.929	34	102	132	2, 5, 17, 31	.032	.032	9	
11	.875 by 26	∞	16,900	4.228	34	122	130	2, 5	.032	.032	9	Speed about one-fourth the speed of sound.
12	.15 by 3	∞	21,500	4.332	44	102	118	Not given	.054	.054	7	
13	2.00 by 48	∞	31,400	4.497	36	107	121	36	.056	.671	10	Open jet tunnel.
14	.55 by 9.8	17.8	15,000	4.279	38	85	66	8.2	.056	.671	10	
15	.55 by 9.8	17.8	30,000	4.477	38	85	66	8.2	.056	.671	10	
16	.55 by 9.8	17.8	60,000	4.778	38	85	66	8.2	.056	.671	10	
17	.55 by 9.8	17.8	85,300	4.931	38 (36)	83	117	8.2	.056	.671	10	

17	.55 by 9.8	17.8	19,400 85,300	4.279 4.931	38 [3] (36)	85 83	66 117	8.2	.056	.071	10	Open jet tunnel.
18	6.00 by 48	8	63,000 94,000	4.799 4.973	35	80	85	Not given.	.125	.125	8	
19	6.00 by 48	8	126,000	5.100	32	85	115	Not given.	.125	.125	8	
20	6.00 by 48	8	173,000	5.238	28	80	242	Not given.	.125	.125	8	
21	7.87 by ?	8	130,000	5.114	31	120	130	Not given.	.025	?	2	Water channel. Values read from small-scale plots.
22	7.87 by ?	8	210,000	5.322	31	42	220	Not given.	.025	?	2	
23	8.9 by 48	8	103,000	5.013	32	130	170	Not given.	.185	.185	4	
24	8.9 by 48	8	126,000	5.100	32	107	177	Not given.	.185	.185	4	
25	8.9 by 48	8	183,000	5.262	31	69	255	Not given.	.185	.185	4	Values read from small-scale plots.
26	8.9 by 48	8	270,000	5.431	31	63	326	Not given.	.185	.185	4	
27	8.9 by 48	8	333,000	5.522	31	56	326	Not given.	.185	.185	4	
28	2.00 by 18	9.0	41,900	4.622	36	50	66	1.1	.042	----------	6	
29	2.00 by 18	9.0	41,900	4.622	57	110	120	1.1	.81	----------	6	Tests for tunnel wall effect by method of images for median section.
30	2.00 by 18	9.0	41,900	4.622	68	66	80	1.1	.85	----------	6	
31	2.00 by 18	9.0	41,900	4.622	86	66	66	1.1	1.00	----------	6	
32	2.00 by 18	9.0	31,400	4.497	39	44	62	Not given.	.042	.016	3	Median section.
33	1.00 by 18	18.0	33,000	4.519	38	95	114	7	.019	.007	1	Single sections about 6 inches from end of cylinder.
34	3.00 by 18	6.0	73,000	4.863	38	57	77	2	.056	.022	1	
35	6.00 by 18	3.0	94,000	4.973	35	65	100	1	.111	.045	1	
36	8.00 by 60	15.0	168,000	5.225	35	67	117	.6	.067	.042	11	
37	8.00 by 60	15.0	252,000	5.401	33	60	178	.6	.067	.042	11	
38	8.00 by 60	15.0	335,000	5.525	31	38	231	.6	.067	.042	11	
39	8.00 by 60	15.0	420,000	5.623	31	39	237	.6	.067	.042	11	Average values over central third of cylinder. Models tested on platform.
40	12.6 by 60	9.6	257,000	5.410	32	38	224	.4	.105	.067	11	
41	12.6 by 60	9.6	385,000	5.585	32	33	251	.4	.105	.067	11	
42	12.6 by 60	9.6	513,000	5.710	32	38	222	.4	.105	.067	11	
43	12.6 by 60	9.6	642,000	5.808	31	43	224	.4	.105	.067	11	
44	.43 by 3.94	9.2	14,900 66,700	4.173 4.824	37 (35)	----------	----------	10.4	.044	.022	10	
45	.71 by 3.94	5.6	24,500 102,000	4.389 5.009	47 (45)	----------	----------	6.3	.072	.036	10	Open jet tunnel, median section values. Each cylinder had 0.24 inch tubes in projection of axis.
46	.79 by 3.94	5.0	27,300 123,000	4.436 5.090	46 (44)	----------	----------	5.7	.080	.040	10	
47	.55 by 3.94	7.2	19,000 85,300	4.279 4.931	42 (40)	55 65	74 87	8.2	.056	.028	10	

[1] Cylinders spanning closed tunnels are assumed to give results applicable to cylinders of infinite length. Cylinders spanning open tunnels are assumed to give results applicable to cylinders of length equal to the diameter of the air stream (serial 15, 16, 17). Cylinders tested on a platform are assumed to give results applicable to cylinders of length equal to twice the length of the cylinder tested (serial 36–43). Cylinders with end plates are assumed to give results applicable to cylinders of infinite length (serial 21,22).

[2] Values in parentheses are corrected for diameter of pressure hole.

Of the 47 observations, 12 are to be discarded for the follow reasons: Serial No. 12 because the speed was about one-fourth speed of sound, and hence an effect of compressibility may expected; serial Nos. 29, 30, and 31 because of the large ratio cylinder diameter to tunnel diameter; serial Nos. 33, 34, and because the measurements were not made at the median sectio and serial Nos. 15, 16, 45, 46, and 47 because of the small ratio length to diameter. For all the undiscarded observations the leng diameter ratio is at least 9, and the three selected [23] characteristi of the distribution of pressure vary but little with that ratio. T relation between the three general characteristics of the distributi and the Reynolds number are shown in Figures 13, 14, and 15. certain correspondence with the curve of drag coefficient in Figu 1 may be noted in the curve (fig. 13) for the angle at which the pr sure equals the static pressure.

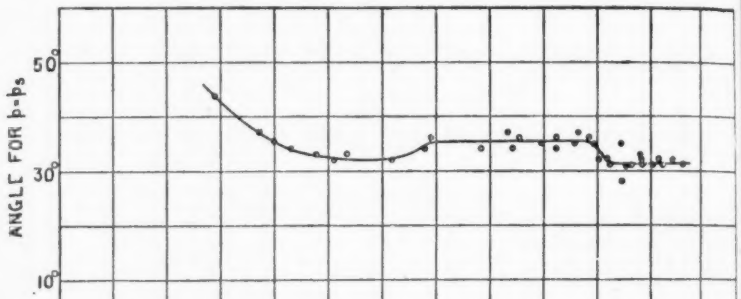

FIGURE 13.—*Effect of Reynolds number upon the angle at which the pressure on an infinite cylinder is equal to the static pressure*

p=pressure on cylinder.
p_s=static pressure.
V=wind speed (ft./sec.).
L=diameter (ft.).
ν=kinematic viscosity (ft.²/sec.)=0.000161 for air. Values from Table 4.

A comparison of our results with the results of Fage and Tayl shows that the critical flow was obtained at lower Reynolds numbe in the British tunnel, a difference to be attributed to the greate turbulence of the British wind tunnel. Taylor's value (serial 2 for the angle at which the pressure equals the static pressure is 2 as compared with our value of 31° (serial 43). We do not kno whether this is to be attributed to the effect of length-diameter rat or to the effect of the ratio of cylinder diameter to tunnel diamete Fage (serials 13 and 32) found a value of 35° for a cylinder of infini length as compared to 39° for a cylinder of length-diameter rat equal to 9 at a Reynolds number of 31,400.

Similar results hold for the mean decrease in pressure behind t cylinder. Above the critical region, Taylor finds 0.8 for the cylinde of infinite length as compared to our mean value of 0.38 for short

[23] The force coefficient varies very rapidly with length-diameter ratio. See Wieselsberger, Physikalis Zeitschrift, 23, p. 219; 1922.

cylinders. Below the critical region, Fage finds 1.02 for the cylinder of infinite length as compared to 0.44 for a cylinder of length-diameter ratio of 9.

There are, however, certain discrepancies, as, for example (serials 13 and 18), between the results of Taylor and Fage at Reynolds

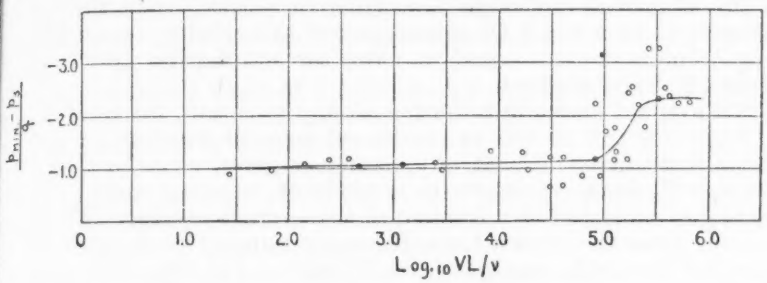

FIGURE 14.—*Effect of Reynolds number upon the minimum absolute pressure on an infinite cylinder*

p_{min}=minimum absolute pressure on cylinder.
p_s=static pressure.
q=velocity pressure.
V=wind speed (ft./sec.).
L=diameter (ft.).
ν=kinematic viscosity (ft.²/sec.)=0.000161 for air. Values from Table 4.

numbers below the critical region, which are probably ascribable to the effect of the ratio of cylinder diameter to tunnel diameter. Moreover, the good agreement between our own results for cylinders of different length-diameter ratios is perhaps a coincidence, the effect of the reduced length-diameter ratio balancing that of the increased ratio of cylinder diameter to tunnel diameter. Due caution must be exercised in applying these results to cylinders of other length-diameter ratios.

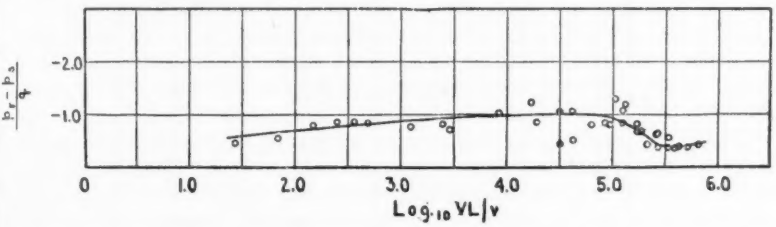

FIGURE 15.—*Effect of Reynolds number upon the mean pressure on the rear of an infinite cylinder*

p_r=mean pressure on the rear.
p_s=static pressure.
q=velocity pressure.
V=wind speed (ft./sec.).
L=diameter (ft.).
ν=kinematic viscosity (ft.²/sec.)=0.000161 for air. Values from Table 4.

It is to be regretted that more information is not available on the effect of length-diameter ratio, especially above the critical region. At Reynolds numbers below the critical, increasing the length-diameter ratio decreases the zonal angle at which the pressure equals the static pressure and also decreases the absolute pressure on the rear of the cylinder. Figure 16 shows the best information avail-

able regarding the effect of the length-diameter ratio on the zero angle at which the pressure equals the static pressure. The data apply to the central part of the cylinder and for Reynolds numbers below the critical. As previously stated, serials 15, 16, and 17 are interpreted as applying to a cylinder whose length is the diameter of the air stream although the cylinders actually span the open-jet air stream, and serial 36 is interpreted as applying to a cylinder of length-diameter ratio equal to twice the actual ratio because of the presence of the platform.

With regard to the distribution along the length, the results shown in Figures 9 and 10 can be condensed into the form of Table 5. In Table 5 the mean C'_D at any section is given as a fraction of the average C_D for the cylinder as a whole or, in other words, the local loading is expressed as a fraction of the average loading. The second column gives the values for a Reynolds number of 168,000 and the third for Reynolds numbers from 335,000 to 642,000. It is seen that the loading is less uniform above the critical region. The greater drag associated with the end loss may be noted.

In most practical applications, the total overturning moment is desired. The distributions shown in Table 5 each give an overturning moment only 1.7 per cent greater than that for a uniform distribution so that the exact distribution along the length need not ordinarily be taken into account.

TABLE 5.—*Distribution of pressure along length*

Height of section above platform, expressed as a percentage of the total length of the cylinder	Average C_D' at section for Reynolds number of 168,000, expressed as fraction of average C_D for cylinder	Average C_D' at section for Reynolds numbers 335,000 to 642,000, expressed as fraction of average C_D for cylinder
99	0.96	1.14
95	1.12	1.33
90	1.11	1.27
80	1.07	1.04
70	1.01	.84
60	.94	.84
50	.94	.84
40	.96	.91
30	.98	1.00
20	.98	1.04
10	.98	1.04
0	.98	1.00

Figure 11, showing the coefficients for the entire cylinder, indicates a difference in turbulence in the several wind tunnels. Taylor's pressure distribution curves indicate a drop at least as early as does Eiffel's.

In the Göttingen results and in ours the force and pressure distribution, respectively, are still changing at the highest Reynolds number. The Reynolds number corresponding to a chimney 20 feet in diameter in a wind of 100 miles per hour is 9,250,000. Extrapolation to such a value can not safely be made from model experiments limited to 642,000.

5. SUMMARY OF MODEL EXPERIMENTS

Measurements have been made of the pressure distribution over cylinders in and above the critical region of Reynolds number. The cylinders were mounted on a platform to simulate chimneys standing on the ground. The measurements show that the changes in the pressure distribution occurring at the critical region are as follows:

1. The zonal angle at which the pressure equals the static pressure decreases from 35° to 31°.

2. The maximum value of the decrease in pressure below the static pressure is doubled, changing from 1.2 times the velocity pressure to 2.4 times the velocity pressure.

3. The mean value of the decrease in pressure over the rear quarter of the cylinder decreases from 0.7 of the velocity pressure to 0.4 of the velocity pressure.

4. The resultant force coefficient decreases to about 0.37.

5. The character of the distribution along the length is such as to give an overturning moment which is about 1.7 per cent greater than that obtained on the assumption of a uniform distribution.

At the highest Reynolds number used in these experiments, the distribution is still changing with the Reynolds number, so that application can safely be made only to small stacks or other cylindrical structures having diameters not significantly exceeding 1 foot.

IV. EXPERIMENTS IN NATURAL WINDS

1. THE INTERPRETATION OF EXPERIMENTS IN NATURAL WINDS

Because the coefficients for cylinders were still changing at the maximum Reynolds numbers attainable in the wind tunnel, attention was given to experiments on large structures in natural winds. Such measurements have a somewhat greater appeal to the engineer than model experiments, although the difficulties of obtaining even reasonably accurate results are very great and the interpretation of observations is a very troublesome matter. The reason for the difficulty is the exceedingly large variability of the wind in intensity and direction. In wind tunnel experiments it is comparatively simple to install a Pitot-static tube and a static plate sufficiently far upstream to be unaffected by the presence or absence of the model. The tube can than be used to give a reference speed and the plate to give a reference pressure. With the model out we can measure the speed and the difference between the static pressure at the place to be occupied by the model and the reference pressure for known values of the reference speed. When the model is put into place we can be reasonably sure of the speed of the wind which strikes it, and of the static pressure at the model, the only error introduced being that due to the finite size of the air stream, which can be minimized by restricting the model area to a small percentage of the tunnel area.

How different is the situation in a natural wind. We can not remove the chimney at will, nor can we control the speed of the wind. If we locate a wind-measuring instrument far away from the chimney, there will be no definite relation between the force on the chimney and the measured wind speed. If we locate the instrument near the chimney, its readings will be affected by the presence of the chimney.

There is no steady reference pressure. The absolute pressure inside a room in a building as well as in the outside air varies with the wind speed.

It occurred to one of us that it would be possible to secure the wind speed from the pressure measurements, if we could find some way of estimating the static pressure. If, for example, we may take the wind-tunnel data of Figure 16 as indicating that the pressure equals the static pressure at a zonal angle of 35°, then the velocity pressure will be equal to the difference between the maximum pressure and the pressure where the angular width of the diagram is 70°, and from that the wind speed may be found by the aid of Table 2. An error of 5° in the zonal angle (2° in the width) corresponds to 5 per cent in the velocity head or to 2½ per cent in the speed. If the angle could be determined within 2°, the force coefficient would be known to within 10 per cent. Since the change in the angle occurring at the critical

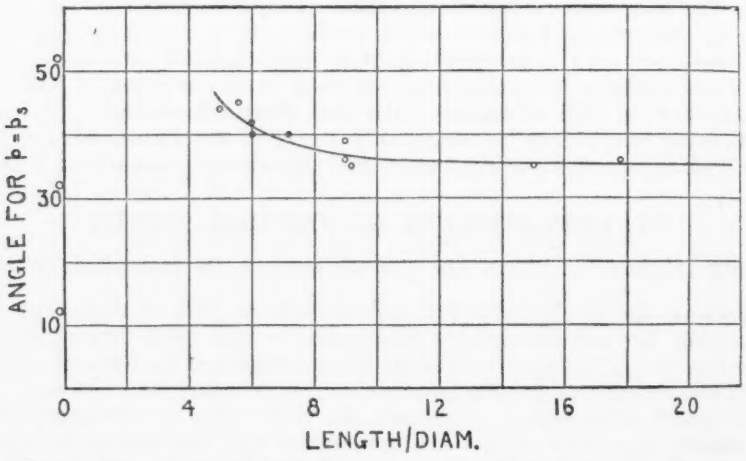

FIGURE 16.—*Angle at which the pressure on cylinders of various length-diameter ratios is equal to the static pressure: Reynolds numbers below the critical*

p = pressure on cylinder.
p_s = static pressure.

region is only 4° and the total change between a length-diameter ratio of 9 and infinity is only 4°, it appears that there is some hope of fixing the angle within 2°.

This method of attack has the advantage of securing a value of the speed of the wind striking the chimney at the level where the measurements are made. It also happens, as will be explained later, that the force coefficient can be obtained from a pressure distribution curve plotted to an arbitrary scale and with an arbitrary reference pressure. The method has the disadvantage that the results of the measurements on the large structure do not stand alone but are interpreted on the basis of a particular kind of extrapolation of data for models, an extrapolation which is, however, far safer than a direct extrapolation of force measurements.

We wish again to point out that this method of treatment of the wind-pressure observations implies the division of the wind-pressure

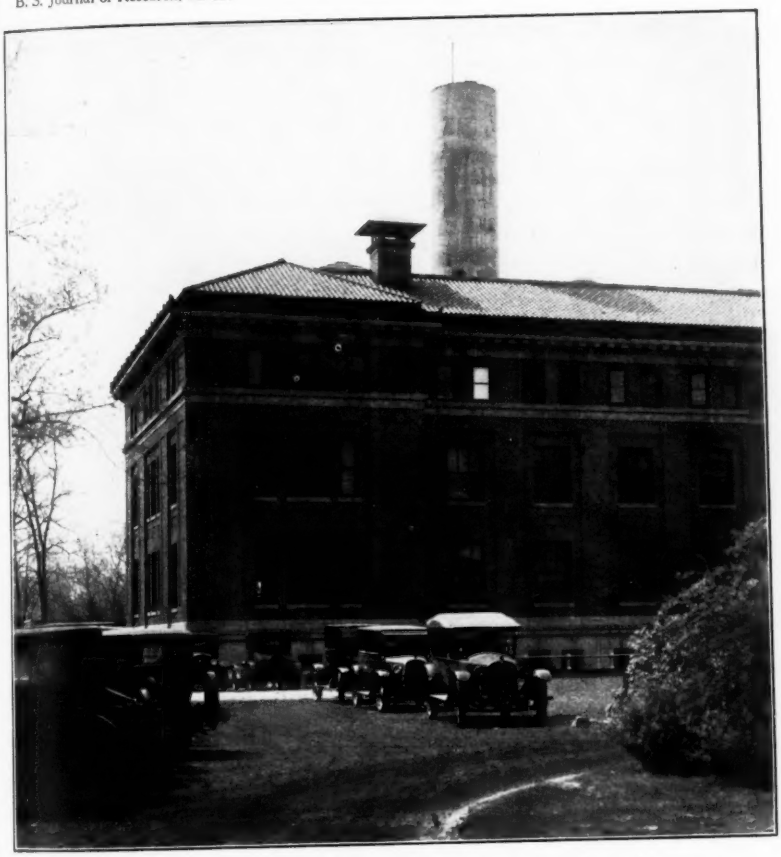

FIGURE 17.—*The 10 × 30 foot experimental stack*

problem as outlined in the introductory section. If it were possible to maintain a continuous record of the pressure on the chimney over a period of several years, a statistical study of the correlation between maximum wind forces and the records of the Weather Bureau station several miles away would seem to give at once the information desired by the engineer. However, the relative exposures of the chimney and the Weather Bureau station would affect the results, and the occurrence of local storms at the two places at different times would so distort the small probabilities, which are of greatest interest, that any general application of the results would be impossible. The analysis suggested in this paper represents an attempt to separate out the effect of the shape of the object from that of the speed of the wind. The object of our observations in natural winds was the determination of force coefficients only, not that of the frequency of occurrence of high winds nor of the relation between mean speed and gust speed.

2. EXPERIMENTS ON A CYLINDRICAL STACK, 10 FEET IN DIAMETER AND 30 FEET HIGH

(a) DISTRIBUTION OF PRESSURE, STACK 10 FEET IN DIAMETER AND 30 FEET HIGH

As the Bureau of Standards was to erect a new power plant chimney on which a more or less permanent installation could be made, it was considered advisable to try the new method on a somewhat smaller scale and under conditions such that the natural wind measurements could be made to stand alone. For this purpose an experimental stack 10 feet in diameter and 30 feet high was erected on the roof of the West Building of the Bureau of Standards. (Fig. 17.) The stack was constructed of a comparatively light timber framework consisting of rings, separated by compression members, to which a sheet metal covering was nailed. The structure was located over a skylight opening, and guy wires were carried inside the structure to the roof beams of the building. At an elevation of about 20 feet above the roof, 24 pressure holes were spaced equally around the circumference. From each hole a separate pipe (three-eighths-inch diameter) was led down the interior of the stack to the observation room in the attic of the building. As first installed, each pressure hole was formed by extending the pipe itself through the sheet metal by a distance of about one-sixteenth-inch and holding the pipe in position by lock washers. It was found that the presence of these small projections produced large suction effects and consequent errors. Wind-tunnel tests showed that the size of the opening (within the limits used) had no large effect. Depression of the hole below the surface gave only small effects, but any projection gave large errors. The pressure holes were then reconstructed by soldering a tube on the inside of the sheet metal covering and drilling from the outside into the tube with a one-thirty second-inch drill. All burrs around the hole were carefully removed.

The 24 pipes were brought together at the observing station with a valve in each line so arranged that all 24 valves could be opened or closed simultaneously by a common operating lever. The valves were of the plug type so that no volume changes occurred on closing them. Each line after passing through its valve led to one tube of a multiple manometer similar to the one which was used for the wind-tunnel tests and which was described in Scientific Paper No. 523.

The other side of the manometer was left open to the air in the observation room. An installation similar to the one used for the experimental stack is shown in Figure 24.

About 10 feet above the top of the stack on the west side a Pitot-static tube was mounted on a wind vane. A sketch of the tube is shown in Figure 18. The pressures from the Pitot and static tubes were led through oil seals to pipes running down to the observation room. The differences between the Pitot and static pressures and the pressure in the observation room were measured on the manometer used to determine the pressure distribution, replacing two stations on the lee side of the stack where the pressure is nearly the same for a number of stations.

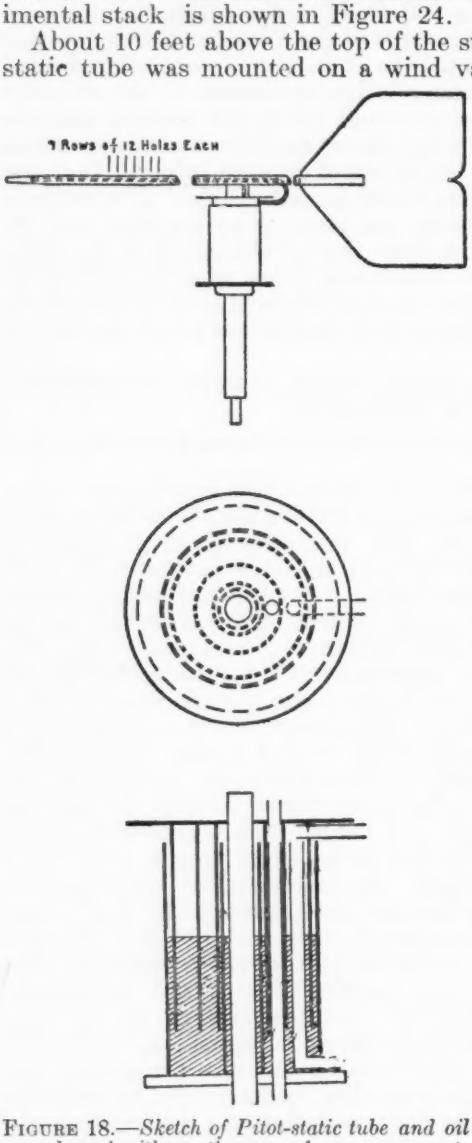

FIGURE 18.—*Sketch of Pitot-static tube and oil seal used with weather vane for measurements of wind speed*

The experimental procedure was as follows: On a day when the wind reached speeds greater than 25 miles per hour, the valves were opened and the observer, watching the fluctuations, closed the valves when the wind speed was reasonably high and steady. Attention was directed to securing the best approximation to steady conditions. The readings of the 24 tubes were then recorded. The valves were again opened and the process repeated some 10 or 12 times.

A typical set of observations is shown in Table 6, in the first two columns.

The observed gauge readings are multiplied by the slope of the manometer (0.196), by the density of the kerosene (0.820), and by a conversion factor (2.045) to obtain the pressure differences in lbs./ft.^{2} These pressure differences are the pressures at the several holes, measured from room pressure as base. From a plot (not shown) of several points near the maximum, the value of the maximum pressure is estimated as well as the angular position at which the maximum occurs. The value of the maximum pressure is then subtracted from all read-

s, giving the amounts by which the pressures at the holes exceed the ximum pressure.[24] The value of the mean excess pressure at the r is then computed, and the ratios to it of the excess pressure at h of the several holes is calculated. These ratios are given in the t column of the table, and in Figure 19 they are plotted with refer- e to the angle as measured from the estimated position of maximum ssure. Curves of this nature may be used to study the similarity of tributions at several speeds and for different cylinders. As the inates of the curve are ratios of pressure differences, the curve is irely independent of the unit in terms of which the pressures are pressed—it is not necessary that they be expressed in lbs./ft.²

TABLE 6.—*Typical observation on experimental stack*

[January 29, 1929 No. 2, Run 1]

gnation of hole (1 is approximately north). umbers run from north to east to south to est	Observed net gauge reading	Pressure difference with room as base pressure	Pressure difference with maximum pressure as base pressure	Ratio of pressure at hole to mean pressure on the rear. Base pressure is maximum pressure
		Lbs./ft.²	*Lbs./ft.²*	
	−13.2	−4.34	−7.81	1.83
	−12.1	−3.98	−7.45	1.75
	−3.3	−1.08	−4.55	1.07
	−1.7	−.56	−4.03	.95
	−2.7	−.89	−4.36	1.02
	−2.0	−.66	−4.13	.97
tatic tube	−.5	−.16		
Pitot tube	9.3	3.05		
	−2.3	−.76	−4.23	.99
	(1)			
	−2.8	−.92	−4.39	1.03
	−2.5	−.82	−4.29	1.01
	−2.8	−.92	−4.39	1.03
	−4.3	−1.41	−4.88	1.15
	(1)			
	−12.3	−4.04	−7.51	1.76
	−9.1	−2.99	−6.46	1.52
	−2.4	−.79	−4.26	1.00
	5.1	1.68	−1.79	.42
	9.5	3.12	−.35	.08
	9.8	3.22	−.25	.06
	5.6	1.84	−1.63	.38
	−1.2	−.39	−3.86	.91
	−8.8	−2.89	−6.36	1.49

[1] Tube leaking badly; readings discarded.

Estimated maximum pressure, 3.47 lbs./ft.² at 9° north of hole 20.
Mean pressure on rear (maximum pressure as base), −4.26 lbs./ft.²=1.17 times velocity pressure from stribution.
Velocity pressure from Pitot, 3.21 lbs./ft.² (35.4 miles per hour).
Velocity pressure from distribution, using static from tube, −3.63 lbs./ft.² (37.6 miles per hour).
Angular separation of points at which the pressure equals static of tube, 69°.

The curve of Figure 19 represents the distribution of pressure round the cylinder, with the maximum pressure, p_{max}, as the refer- nce pressure and the difference between the maximum pressure $_{max}$ and the pressure on the rear p_r as the unit of pressure. The ext step is to determine the average force per unit length exerted

[24] The absolute pressure at the holes is less than the maximum pressure. The "excess pressure," there- re, has a negative sign as shown in the fourth column of Table 6.

upon this section of the cylinder and in a direction parallel to the wind, namely

$$\int \frac{p - p_{max}}{p_r - p_{max}} \sin\theta ds = \int \frac{p_{max} - p}{p_{max} - p_r} dw$$

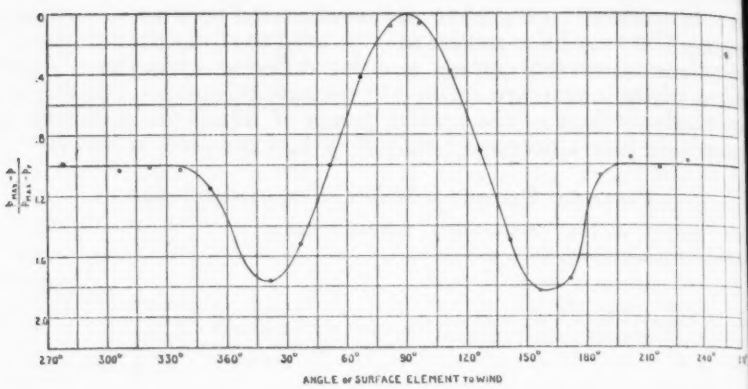

FIGURE 19.—*Pressure distribution on experimental stack, sample run of Table 6*

p = pressure at station.
p_{max} = maximum absolute pressure on stack.
p_r = mean pressure on rear quarter.

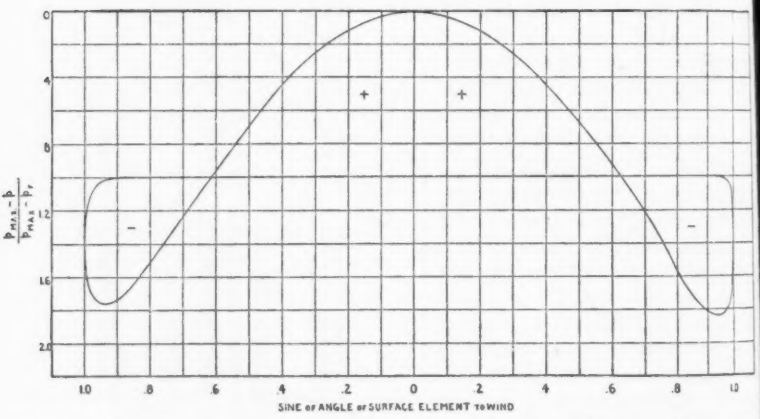

FIGURE 20.—*Plot for use in integrating the pressure distribution of Figure 19 so as to get the resultant mean pressure at section*

p = pressure at station.
p_{max} = maximum absolute pressure on stack.
p_r = mean pressure on rear quarter.

where θ is the angle of the surface element to the wind, ds is an element of the circumference and dw is an element of the projection of the surface element on a plane normal to the wind; $\sin\theta ds = dw$, and it is obvious that

$$\frac{p - p_{max}}{p_r - p_{max}} = \frac{p_{max} - p}{p_{max} - p_r}$$

The integration may be performed graphically with the aid of Figure 20. Dividing the integral by the diameter (w) of the cylinder, the

rage wind force per unit area at this section is obtained in terms $p_{max}-p_r$ as unit. For the example used, a value of 0.22 is obtained. Attention is again called to the fact that this value is arrived at, or n be arrived at, from a plot of the pressure distribution on any bitrary scale and with any arbitrary reference pressure to begin th; that is, from readings on a manometer of any slope (so long all tubes have the same slope) and with its reservoir connected any reference pressure. If, as in the experiments described, the locity pressure is measured on the same manometer, we may deter- ne at once the ratio of $p_{max}-p_r$ to the velocity pressure (1.17 in e example) and hence obtain the true force coefficient (1.17×0.22 0.26) without any knowledge of the slope of the manometer. Or, from Table 4 we estimate the probable value of the zonal angle at hich the pressure is equal to the static pressure as 31° for a cylinder infinite length at Reynolds numbers above the critical region, and we estimate from Figure 16 that the correction to a length-diameter tio of 6 is 6°, obtaining a probable value of 37°, we may proceed as llows. From the estimated value of the zonal angle (37°) the gular width of the distribution curve at such an ordinate that the essure equals the static pressure is estimated to be 74°. From gure 19, this angular width corresponds to

$$\frac{p_{max}-p}{p_{max}-p_r}=0.95$$

t at this ordinate, $p=p_s$, and hence $p_{max}-p=p_{max}-p_s=$ the velocity essure q. Thus $\frac{q}{p_{max}-p_r}=0.95$ or $\frac{p_{max}-p_r}{q}=1.05$ and the true shape efficient is $1.05\times 0.22=0.23$. This last procedure is illustrative ly. We have so little information as to the effect of length- ameter ratio above the critical region that predictions for short linders are uncertain. Furthermore the experimental chimney 0 feet in diameter and 30 feet high is not mounted on an infinite ane but on top of a building and its effective length-diameter ratio hard to determine. Actually the zonal angle obtained by use of e static tube readings is 34.5° which corresponds to an effective ngth-diameter ratio of about 7½ using the procedure indicated above. The method which has been outlined for reducing the observations ay appear somewhat indirect and cumbersome. Its object is to stpone all uncertainties until the last step, namely, until the termination of the ratio $(p_{max}-p_r)/q$ or its equivalent, the deter- ination of the zonal angle at which the pressure equals the static ressure.

) OVERTURNING MOMENT, STACK 10 FEET IN DIAMETER AND 30 FEET HIGH

The measurement of the pressure distribution at a given elevation ives information as to the average wind load at that elevation only. t tells nothing about the actual overturning moment exerted by the ind. It seemed desirable to attempt to measure that directly. The ethod employed is indicated schematically in Figure 21. The stack as supported at four points at the corners of a square, the sides of hich run north and south and east and west, and means were pro- ided, as explained later, for measuring the reactions at the four

points. When no wind is blowing, the reactions will be caused sole by the weight of the stack. When the wind blows, the reactions change. We shall assume that t effect of the wind in overturn the chimney is equivalent to t effect of a force F acting at t center of the projected area of t chimney, which is at an elevati h, above the plane containing t points of application of the re tions at the base. We shall call t increase in the reaction at the nort west corner, R_{NW}, the othe R_{NE}, R_{SE}, and R_{SW} and shall rega them as positive when the upwa reaction on the cylinder increas and hence the downward force the measuring apparatus increas The length of the diagonal of t square is called $2a$. Resolving t wind force into components p allel to the diagonals of the s square as indicated in Figure 2 and taking moments about each the diagonals in turn, we find

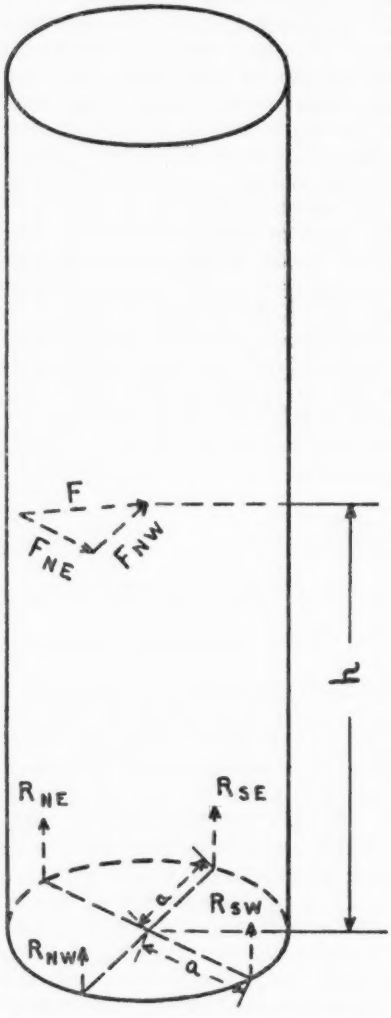

FIGURE 21.—*Diagram illustrating how the wind force on the experimental stack was computed from the measured reactions at four points of support*

F=wind force.
F_{NE}=component of wind force in *NE-SW* direction.
F_{NW}=component of wind force in *NW-SE* direction.
h=height of center of stack above the plane of the four supports.
$2a$=distance between *NE* and *SW* or *NW* and *SE* supports.
R_{NE}=upward reaction on cylinder at *NE* support.
R_{SE}=reaction at *SE* support.
R_{SW} at *SW* support, and R_{NW} at *NW* support.

$$F_{NE}h=(R_{SW}-R_{NE})a$$

$$F_{NW}h=(R_{SE}-R_{NW})a$$

The total force, F, is given by

$$F=\sqrt{F_{NW}^2+F_{NE}^2}$$

and its azimuthal angle, α, fro the meridian

$$\alpha=315°+\tan^{-1}\frac{F_{NE}}{F_{NW}}$$

The force coefficient C_D is given b

$$C_D=\frac{F}{Aq}$$

where A is the projected area of t stack (300 ft.^{2}) and q is the veloci pressure.

The reactions were measured b the use of pressure capsules o the sylphon type (metal bellows The sylphons were connected t

urdon tube pressure gauges by pipe lines, each system of sylphon, ping, and gauge being filled with kerosene. Each pressure gauge s calibrated by comparison with a mercury column, and each lphon and gauge system was calibrated in a compression testing chine to determine the effective area of the sylphon. When talled under the stack, each pipe line contained a valve, and the r valves were connected to a common operating lever. This was ring operated, the trigger being released by the lever which operated e valves in the pipe lines for pressure-distribution measurements. rangements were provided for equalizing the pressures at any time d for refilling so as to replace any slight leakage at the valves.

The lateral force on the stack was taken by a system of tension res approximately in the plane of the top of the sylphons. During easurements of the overturning moment, the guy wires were ckened. The stack was not originally designed to be supported at r points and the necessary inclusion of the points within the linder reduced the stabilizing moment of the weight of the stack. s a result of continued racking by the wind and the decreased sistance to overturning caused by the four-point support, the stack as blown from the roof on March 7, 1929, fortunately without rious damage to the building. The wind gusts at that time exceeded true wind speed of 60 miles per hour.

Table 7 shows a typical group of readings and the method of duction. The chief experimental difficulties were due to the ability of the observer to shut off the wind so as to obtain zero adings. The sylphons moved very little under different loads, and ach could be made to take any fraction of the total load within wide mits by controlling the quantity of kerosene in the system. It as necessary therefore to equalize the pressures in the four sylphons, t a time when there was no wind, by the simple device of inter-onnecting them. The pressures could not be exactly equalized since he center of gravity of the stack was not exactly at the intersection f the diagonals of the square of the supporting sylphons.

TABLE 7.—*Typical set of observations on overturning moment*

[h=14.33 feet, a=3.98 feet, effective area of sylphon=97 in.^{2}]

Sylphon		NW	NE	SE	SW
ero (no wind)	lbs./in.^{2}	13.6	12.8	14.9	15.0
eading	do	7.1	13.9	20.8	12.0
et pressure	do	−6.5	1.1	5.9	−3.0
eactions	pound	−630	107	572	−291

Hence

$$F_{NE}=\frac{(-291-107)3.98}{14.33}=-111 \text{ pounds}$$

$$F_{NW}=\frac{(572+630)3.98}{14.33}=334 \text{ pounds}$$

$$F=\sqrt{334^2+111^2}=353 \text{ pounds}$$

From Table 6, q from distribution $=3.63$ lbs./ft.^{2}. Hence $\frac{}{}$ $=\frac{353}{3.63\times 300}=0.32$. $\alpha=315°+\tan^{-1}\frac{-111}{334}=315°-18°=297°$ as co

pared with 289° from the distribution. Owing to a small amou of leakage and to some creeping of the sylphons under load (the th metal of the bellows was loaded somewhat above the elastic limi the zero readings showed a certain amount of drift which could on be checked by observations when there was no wind. The erro introduced can not, in general, exceed 10 per cent and are probably the order of 5 per cent.

(c) SUMMARY, STACK 10 FEET IN DIAMETER AND 30 FEET HIGH

Table 8 contains a summary of all observations of the overturni moment and the derived force coefficients, together with the da taken simultaneously on the pressure distribution. The table al contains the readings obtained from the Pitot-static tube. Throug out the table the static pressure is that obtained from the stat connection of the Pitot-static tube. The velocity pressure used the computation of force coefficients is that obtained from the ma mum pressure on the cylinder and the static pressure from th Pitot-static tube. Column 8 of the table shows that the wind spe as obtained from the Pitot-static tube is on the average nearly th same as that obtained from the maximum pressure on the cylind and the static pressure from the Pitot-static tube.

TABLE 8.—*Summary of results on experimental stack*

TABLE 8.—*Summary of results on experimental stack*

Date	Maximum pressure referred to pressure in attic	Pitot pressure referred to pressure in attic	Static pressure referred to pressure in attic	Velocity pressure from distribution column 1—column 3	Velocity pressure from Pitot, column 2—column 3	Wind speed from distribution column 4	Wind speed from Pitot, column 5	Ratio of column 7 to column 6	Wind direction from distribution (azimuthal angle from N)	Wind direction from sylphons	Column 9—column 10	Width of distribution curve at ordinate equal to column 4 from maximum	Average pressure on rear referred to maximum pressure	Col. 13 / Col. 4	Force coefficient from distribution referred to pressure on rear	Column 15 × column 14 force coefficient from distribution referred to velocity pressure from distribution	Force coefficient from sylphons referred to velocity pressure from distribution
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
	Lbs./ft.²	*Lbs./ft.²*	*Lbs./ft.²*	*Lbs./ft.²*	*Lbs./ft.²*	*M. p. h.*	*M. p. h.*		°	°	°	°					
April 28, 1928	2.04	1.84	0.10	1.94	1.74	27.5	26.1	0.949	270	245	25						0.50
	2.81	2.73	.07	2.74	2.66	32.7	32.2	.984	296	322	−26						.40
	2.23	3.55	.20	2.03	3.35	28.1	36.1	1.284	294	337	−43						.60
	3.48	3.48	−.03	3.51	3.51	37.0	37.0	1.000	276	275	1						.44
	2.06	2.04	.00	2.06	2.04	28.4	28.2	.992	291	297	−6						.39
	1.43	2.33	.00	1.43	2.33	23.6	30.2	1.280	301	284	17						.39
	3.30	3.42	.00	3.30	3.42	35.7	36.5	1.022	291	330	−39						.45
	1.85	1.64	.00	1.85	1.64	26.9	25.3	.941	264	264	0						.44
	2.00	1.81	.00	2.00	1.81	27.9	26.6	.953	290	286	4						.40
	2.16	2.14	.03	2.13	2.11	28.8	28.7	.997	270	285	−15						.32
	2.10	2.10	.07	2.03	2.03	28.1	28.1	1.000	284	294	−10						.37
	3.17	3.19	.07	3.10	3.12	34.8	34.9	1.003	286	271	15						.43
	3.86	3.22	.07	3.79	3.15	38.5	35.1	.912	306	310	−4						.33
	3.00	2.86	.07	2.93	2.79	33.8	33.1	.979	302	314	−12						.42
	2.80	2.86	.07	2.73	2.79	32.6	33.1	1.015	288	253	35						.39
	2.76	2.70	.07	2.69	2.63	32.4	32.0	.988	291	254	37						.36
November 8, 1928	3.43	3.72	−.20	3.63	3.92	37.6	39.1	1.040	300	324	−24	77	4.08	1.12	0.254	0.28	.41
	2.58	2.73	.00	2.58	2.73	31.7	32.7	1.032	278	281	−3	77	3.13	1.21	.215	.26	.36
	3.17	4.11	−.03	3.20	4.14	35.3	40.2	1.138	315	298	17	71	3.96	1.24	.217	.27	.39
	2.90	3.42	.03	2.87	3.39	33.5	36.4	1.087	295	300	−5	69	3.64	1.27	.211	.27	.46
	4.44	4.74	.33	4.11	4.41	40.0	41.5	1.038	298	273	25	69	5.23	1.27	.230	.29	.47
	3.69	3.42	.26	3.40	3.16	36.4	35.1	.964	299	304	−5	71	4.21	1.24	.202	.25	.42
	2.13	2.33	.10	2.03	2.23	28.1	29.5	1.050	297	288	9	81	2.78	1.37	.197	.27	.44
	2.30	2.37	.07	2.23	2.30	29.5	30.0	1.017	289	289	0	66	2.85	1.28	.236	.30	.39
	2.11	2.53	.16	1.95	2.37	27.6	30.4	1.102	293	290	3	67	2.56	1.31	.204	.27	.39
	1.93	2.04	−.03	1.96	2.07	27.6	28.4	1.028	306	315	−9	69	2.44	1.24	.257	.32	.43
	1.96	2.14	−.03	1.99	2.17	27.9	29.1	1.043	309	315	−6	72	2.56	1.29	.229	.30	.44
	1.51	1.55	−.07	1.58	1.62	24.8	25.1	1.012	294	304	−10	71	1.97	1.25	.250	.31	.34

Pressure distribution taken with projections around holes and is therefore omitted.

TABLE 8.—*Summary of results on experimental stack*—Continued

Date	Maximum pressure referred to pressure in attic	Pitot pressure referred to pressure in attic	Static pressure referred to pressure in attic	Velocity pressure from distribution column 1—column 3	Velocity pressure from Pitot, column 2—column 3	Wind speed from distribution column 4	Wind speed from Pitot, column 5	Ratio of column 7 to column 6	Wind direction from distribution (azimuthal angle from N)	Wind direction from sylphons	Column 9—column 10	Width of distribution curve at ordinate equal to column 4 from maximum	Average pressure on rear referred to maximum pressure	Col. 13 / Col. 4	Force coefficient from distribution referred to pressure on rear	Column 15 ×column 14 force coefficient from distribution referred to velocity pressure from distribution	Force coefficient from sylphons referred to velocity pressure from distribution
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
	Lbs./ft.²	*Lbs./ft.²*	*Lbs./ft.²*	*Lbs./ft.²*	*Lbs./ft.²*	*M. p. h.*	*M. p. h.*		°	°	°	°					
January 23, 1929	2.27	2.27	−.10	2.37	2.37	30.0	30.0	1.000	281	278	3	73	2.86	1.21	0.240	0.29	0.30
	1.95	1.29	−.07	2.02	1.36	28.1	23.0	.819	275	275	0	71	2.63	1.30	.252	.33	.36
	1.43	1.29	−.03	1.46	1.32	23.9	22.7	.950	303	315	−12	72	1.86	1.27	.227	.29	.33
	1.84	1.91	.00	1.84	1.91	26.8	27.3	1.018	279	300	−21	71	2.27	1.23	.215	.26	.40
January 29, 1929, p. m.	3.47	3.05	−.16	3.63	3.21	37.6	35.4	.941	294	297	−3	69	4.26	1.17	.218	.26	.32
	3.68	3.75	−.03	3.71	3.78	38.0	38.4	1.010	284	308	−24	72	4.38	1.18	.239	.28	.36
	4.42	5.42	.07	4.35	5.35	41.2	45.7	1.109	290	273	17	69	5.16	1.19	.211	.25	.36
	3.87	3.38	.07	3.80	3.31	38.5	36.0	.935	306	308	−2	68	4.67	1.23	.201	.25	.30
	3.75	4.38	−.07	3.82	4.45	38.6	41.7	1.080	294	302	−8	70	4.65	1.22	.198	.24	.38
	3.89	3.68	.14	3.75	3.54	38.3	37.2	.971	294	306	−12	71	4.77	1.27	.249	.32	.31
	4.10	4.04	.07	4.03	3.97	39.7	39.4	.992	291	298	−7	70	4.70	1.17	.200	.23	.31
	3.43	4.35	−.17	3.60	4.52	37.5	42.0	1.120	284	283	1	67	4.56	1.27	.188	.24	.35
	3.81	3.98	.00	3.81	3.98	38.6	39.4	1.020	299	306	−7	68	4.82	1.27	.217	.28	.38
	4.63	4.08	−.07	4.70	4.15	42.8	40.3	.942	304	331	−27	71	5.58	1.19	.218	.26	.39
	3.87	4.54	−.14	4.01	4.68	39.6	42.7	1.077	299	315	−16	72	4.70	1.17	.214	.25	.33
	4.54	4.40	−.07	4.61	4.47	42.4	41.8	.986	290	292	−2	65	5.80	1.26	.227	.29	.36
January 29, 1929, a. m.	2.79	2.93	−.10	2.89	3.03	33.6	34.4	1.023	296	305	−9	69	3.70	1.28	.236	.30	.41
	2.88	2.66	−.10	2.98	2.76	34.1	32.8	.962	296	305	−9	71	3.66	1.23	.243	.30	.37
	3.72	3.42	−.17	3.89	3.59	39.0	37.5	.961	304	309	−5	69	4.61	1.18	.213	.25	.36
	4.12	3.76	−.14	4.26	3.90	40.8	39.0	.956	314	331	−17	71	5.15	1.21	.220	.27	.34
	3.91	4.52	−.17	4.08	4.69	39.9	42.8	1.072	308	315	−7	71	5.02	1.23	.260	.32	.35
	3.77	3.76	−.14	3.91	3.90	39.1	39.0	.998	312	340	−28	71	4.61	1.18	.217	.26	.31
	3.14	3.35	.03	3.11	3.32	34.9	36.0	1.031	284	291	−7	68	3.95	1.27	.230	.29	.35
	3.30	3.17	−.14	3.44	3.31	36.6	36.0	.983	302	327	−25	68	4.25	1.24	.211	.26	.38
	2.86	3.28	−.17	3.03	3.45	34.4	36.7	1.067	281	279	2	71	3.65	1.20	.213	.26	.32
	4.42	4.55	.14	4.28	4.41	40.9	41.5	1.014	302	315	−13	68	5.39	1.26	.233	.29	.37
	5.10	5.80	.00	5.10	5.80	44.6	47.6	1.067	287	289	−2	68	6.10	1.20	.206	.25	.28
	3.39	4.11	−0.10	3.49	4.21	36.9	40.6	1.100	281	267	14	70	4.28	1.23	0.217	.27	.32
	Mean values							1.019 ±0.050				79°.4 ±2°.8		1.24 ±0.04	0.223 ±0.015	.28 ±.02	.30 ±.04

Column 12 shows a mean width of the distribution curve at the level of the static pressure as $70.4° \pm 2°$; the zonal angle is therefore 35°. The value estimated from the little information available on short cylinders by assuming the same relative effect of length-diameter ratio above the critical region of Reynolds numbers as observed below the critical region and by assuming the effective length-diameter ratio to be the same as if the cylinder were standing on an infinite plane surface, is 37°. The use of this estimated value would lead to force coefficients about 10 per cent lower than those given. The cylinder does not stand on an infinite plane surface, and its effective length-diameter ratio is therefore somewhat greater than 6.

Column 16 shows the mean force coefficient obtained from the distribution to be 0.28 ± 0.02, while that obtained from the overturning moment is 0.39 ± 0.04. The local loading at an elevation of two-thirds the height is therefore only about three-fourths the average loading on the whole stack. This is a somewhat greater difference than that shown in Figure 10 for the model experiments on cylinders of somewhat greater length-diameter ratios. It may be remarked that possible errors in the determination of the velocity pressure do not affect the relative values of the force coefficients, since the same value is used for the determination of the coefficients from the distribution and from the overturning moment. The greater difference between the two values for the experimental stack is probably associated with the smaller length-diameter ratio.

The value of 0.39 corresponds to a mean pressure on the projected area of the cylinder of 10 lbs./ft.^{2} at a wind speed of 100 miles per hour. This figure is about one-half that commonly used in the design of chimneys. However, chimneys are much taller in proportion to their diameter than the experimental stack, and, therefore the results obtained on the short stack can not be applied to chimneys without some further justification. The object of the measurements on the experimental stack was to test a method of procedure for measurements on an actual chimney. The results of the test are reasonably satisfactory when the attendant circumstances are considered.

3. POWER PLANT CHIMNEY

On the occasion of the construction of a new power plant at the Bureau of Standards, provision was made for measuring the distribution of wind pressure on the stack at a single elevation, so that some information might be obtained as to the wind pressure on an actual chimney. The chimney is of radial brick, 200 feet from the foundation to the top of the chimney, the internal diameter at the top being 10 feet. The foundation is, however, considerably below the street level, and the top of the chimney is only about 120 feet above the highest part of the power plant building. A view of the stack and its surroundings taken from the East Building of the bureau and looking toward the northwest is shown in Figure 22, and a drawing is given in Figure 23. The parapet on the Northwest Building (the one to the left in fig. 22), on which the tower and wind vane are mounted, is about 88 feet below the top of the chimney. The elevation selected for the pressure observations is about 41 feet below the top, the external diameter of the chimney at this point being 11.8 feet.

The dark line in Figure 22 running down the south side of the stac is caused by the group of 24 three-eighth inch brass pipes connecting the pressure holes with the observing room in the building. Th pipes are under the ladder, which does not show in the reproduction. The pressure openings are located in a plane 2 feet above the top o the dark line, in a wide mortar joint indicated in the figure. A pipe

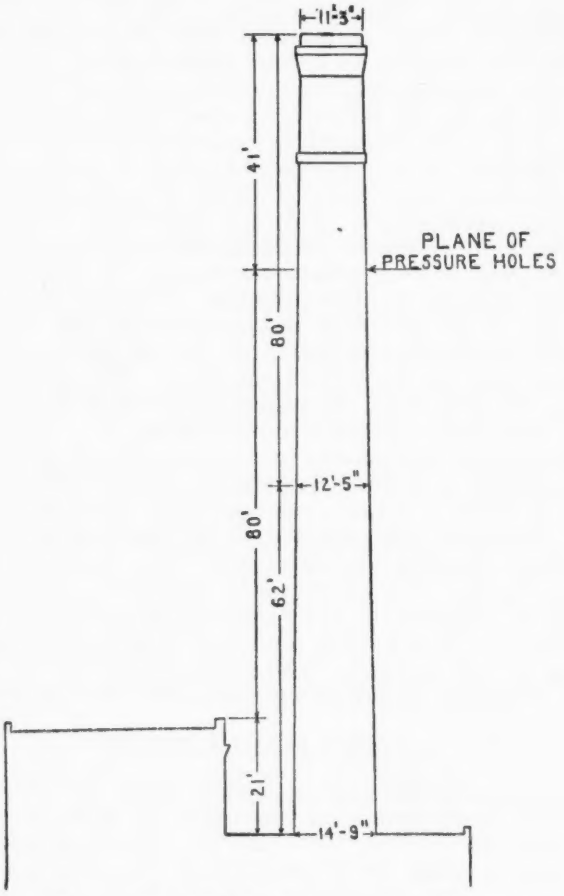

FIGURE 23.—*Sketch of power plant chimney showing principal dimensions*

runs from each opening to the interior of the chimney, thence around the inside of the chimney and down to the point of assembly, where all are brought outside and down under the ladder. The openings are simply the squared off ends of the three-eighth inch pipes. Precaution was taken to have no projections, the installation being supervised by one of the authors. The area around the pipes was pointed up. Notwithstanding these precautions the surface of the chimney is not a smooth surface, even around the holes, but in view of our experience with the experimental stack and with a model of

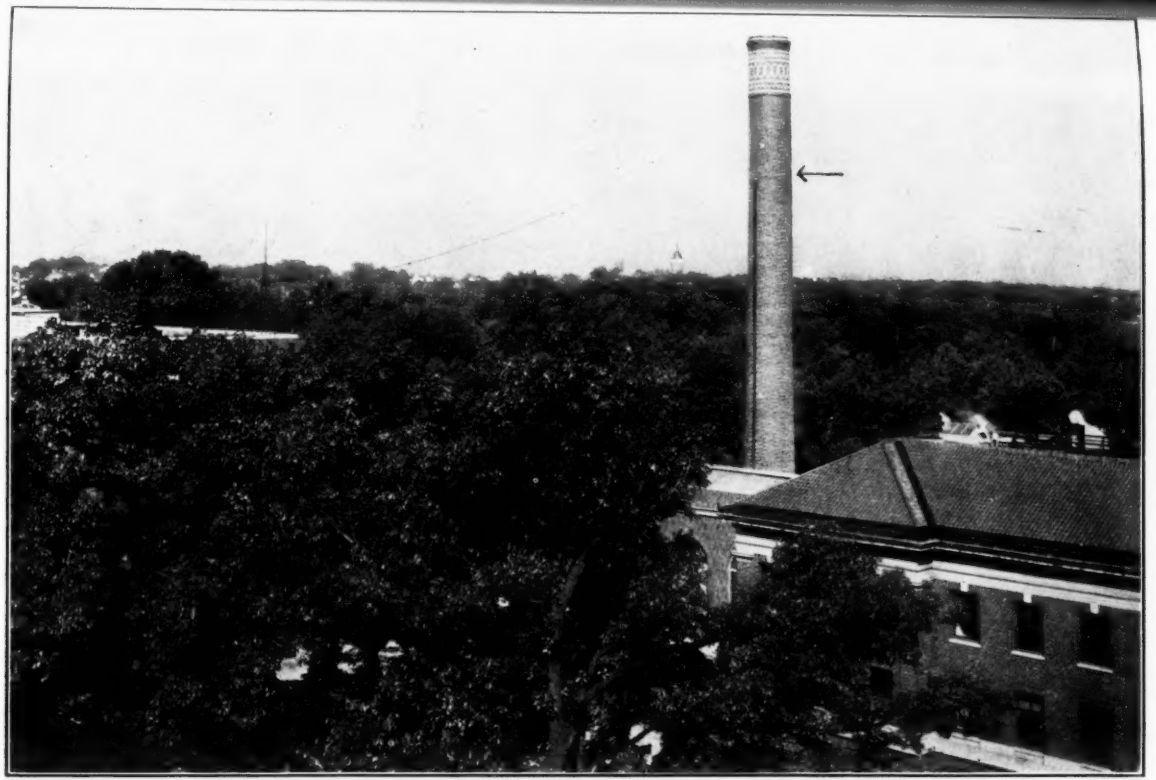

FIGURE 22.—*The power plant chimney of the Bureau of Standards looking toward the northwest, the direction from which come the strongest winds*

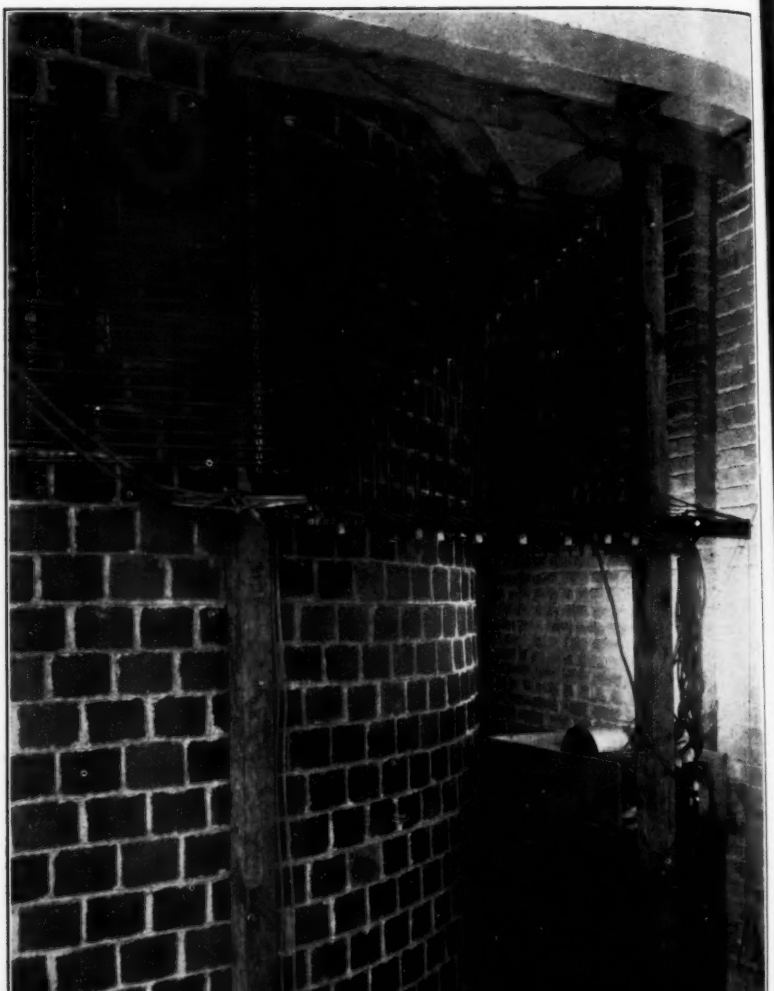

FIGURE 24.—*The observer's station on the power plant chimney*

part of the surface in the wind tunnel, the errors are not believed be very great.

Besides the ladder running down the south side of the chimney d the 24 pipes, there is another projection on the north side, a htning conductor leading from the lightning rods at the top of the imney to the ground. The stack is slightly tapered as indicated Figure 23, and there are certain projections in connection with the namentation at the top. The chimney is not, therefore, exactly circular cylinder, its surface is not smooth and, in view of the rrounding topography (fig. 22), a determination of its effective ngth-diameter ratio is somewhat difficult. We may perhaps esti- ate the effective length-diameter ratio as roughly 15 to 20, consider- g the chimney as equivalent to a 100-foot stack standing on an finite plane surface. From Table 4 and Figure 16 we would then stimate the zonal angle at which the pressure equals the static ressure as 31°.

An attempt was made to secure independent checks of the wind peed by means of a Pitot-static tube (the same used on the experi- ental stack and shown in fig. 18) mounted on a tower on the North- est Building. (See fig. 22.) The Pitot-static tube was approximately 30 feet horizontally from the chimney and some 20 feet below the levation of the pressure holes. The gauge was installed in the Northwest Building, and an electrically operated shut-off valve was onnected to the trigger mechanism on the pressure distribution pparatus. Repeated series of observations have shown only a hance relation between the speed at the chimney and the speed at he wind gauge. One speed may be zero when the other is a maxi- num, or the two may occasionally vary together. In the case of the xperimental stack where the wind gauge was only 20 feet from the ressure holes, the correlation was good. At six times this distance, here is no relation between the two speeds. The observing station s very similar to that described for the experimental stack. It is hown in Figure 24. The details of the mechanism do not show very learly since one sees the 24 operating levers end on. The details f operation and of computation were the same as described for the xperimental stack. In general, however, the results have been com- uted in the form of averages of groups of points. A typical plot of group of observations is shown in Figure 25.

The result of some nine groups of observations gives an average alue of 0.37 ± 0.02 for the ratio of the average force per unit area f the projection to the pressure difference between the lee side of the himney, p_r, and the maximum pressure p_{max}. Assuming the zonal ngle at which the pressure is equal to the static pressure to be 31°, he ratio of $p_{max} - p_r$ to the velocity pressure is found to be 1.82, and hence the true shape coefficient $1.82 \times 0.37 = 0.67$, a value corre- sponding to a pressure of 17.1 lbs./ft.^{2} at a true wind speed of 100 miles per hour. This value is considerably higher than the value obtained on the short cylinder, a fact to be attributed mainly to the greater length-diameter ratio, but probably to some extent to the greater roughness of the actual chimney.

V. RÉSUMÉ

In Figure 26 we have plotted for comparison the distributio around the 12.6-inch cylinder at section 6 obtained in the wind tunn

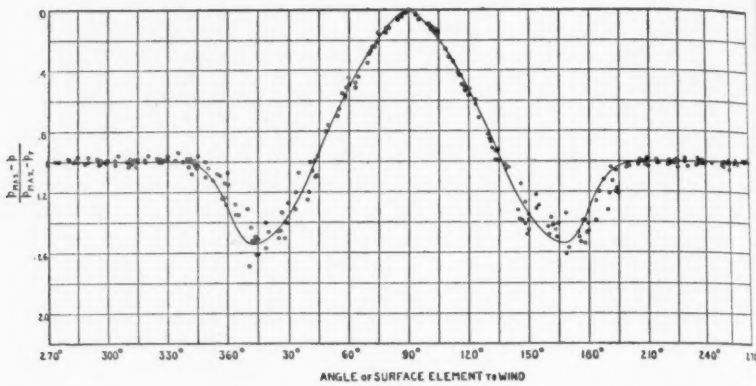

FIGURE 25.—*Pressure distribution 41 feet from the top of the power-plant chimney, group of 12 runs*

p = pressure on chimney.
p_{max} = maximum absolute pressure on chimney.
p_r = mean pressure on rear quarter of chimney.
All 41 feet from the top.

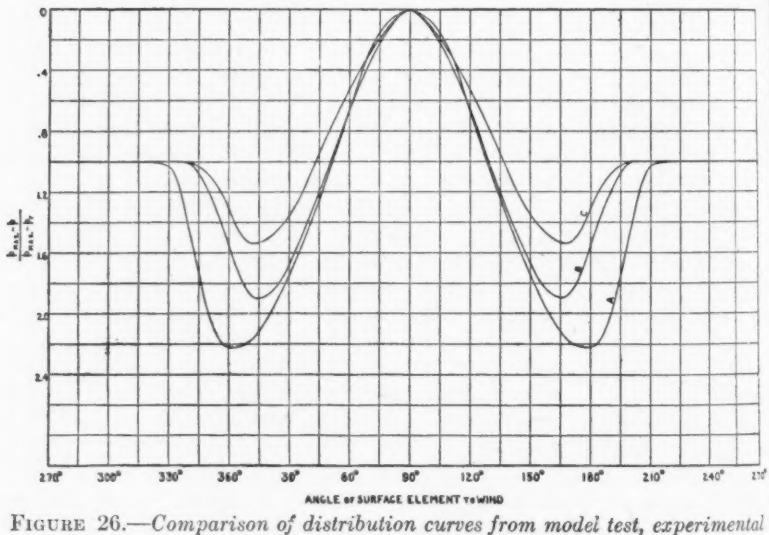

FIGURE 26.—*Comparison of distribution curves from model test, experimental stack, and power-plant chimney*

p = pressure on chimney.
p_{max} = maximum absolute pressure on chimney.
p_r = mean pressure on rear quarter.
A, 12.6-inch cylinder in wind tunnel, distance from top = 1.4 diameters.
B, 10 by 30 foot experimental stack, distance from top = 1 diameter.
C, power-plant chimney, distance from top = 3.6 diameters.

at a speed of 80 ft./sec., the distribution around the 10 by 30 feet experimental stack, and the distribution around the power plant chimney, all expressed in terms of the difference between the pressure

the lee side and the maximum pressure. In Figure 27, the same ves are given in terms of the velocity pressure, known in the cases the 12.6-inch cylinder and the 10 by 30 foot stack, but for the wer plant chimney obtained on the assumption of a zonal angle of ° for the point at which the pressure equals the static pressure. e distributions are of the same general nature but very considerably ferent in detail.

The general conclusions to be drawn from our work are as follows:

1. The wind pressure on a chimney at a given wind speed is a function of the ratio of the height of the chimney to its diameter and ssibly also of the roughness of its surface.

2. Model experiments can not be directly utilized in determining e force coefficients on chimneys because of the large effect of the e and speed as combined in the Reynolds number.

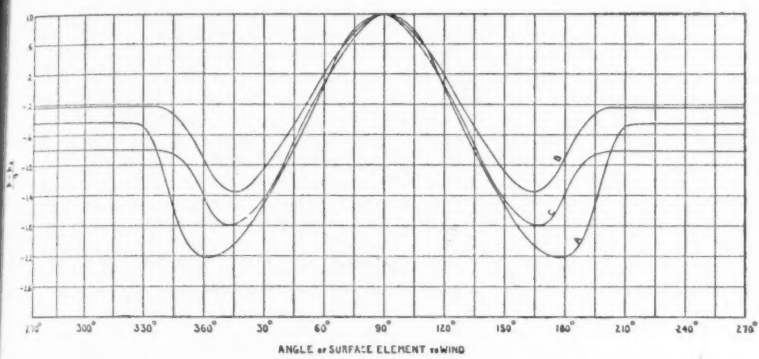

FIGURE 27.—*Comparison of distribution curves from model test, experimental stack, and power plant chimney*

p=pressure on chimney.
p_s=static pressure, q= velocity pressure. For the power-plant chimney (curve C), p_s is assumed to be equal to the value of p at the zonal angle 31°.
A, 12.6-inch cylinder in wind tunnel, distance from top=1.4 diameters.
B, 10 by 30 foot experimental stack, distance from top=1.0 diameter.
C, power-plant chimney, distance from top=3.6 diameters.

3. A wind pressure coefficient corresponding to 20 lbs./ft.^{2} of projected area at a wind speed of 100 miles per hour is a safe value for use in designing chimneys of which the exposed height is of the order of ten times the diameter and a reduction below this figure does not seem to be justified in the light of the results of our experiments when allowance is made for the fact that the pressure was measured at a single elevation.

4. Locally, the pressure may reach large values. This may need to be considered in the design of thin walled stacks of large diameter.

5. Further experiments are necessary for obtaining satisfactory information as to the variation of wind pressure with the ratio of height to diameter.

WASHINGTON, March 26, 1930.

THERMOMETRIC LAG OF AIRCRAFT THERMOMETERS, THERMOGRAPHS, AND BAROGRAPHS

By H. B. Henrickson

ABSTRACT

A constant which will be called the time lag has been determined experimentally r thermographs, barographs, and of the temperature element of a Fergusson eteorograph. When the instruments are exposed in the same medium and to e same ventilation this constant can be used to evalute their thermometric lag. or the purpose of comparison this constant was also measured for a number of boratory thermometers. The tests on the thermometers and thermographs ere made in an air stream of 17 m. p. h. and those on the barographs in still air d in an air stream of 10 m. p. h. Results for the thermometers show that the quid-filled type has the greatest time lag and therefore under similar conditions exposure the greatest thermometric lag, followed in order by the bimetallic strip pe and the electric resistance thermometers. All of the barographs, even the etal-cased types, have a far greater time lag than the thermometers, but the lag reduced considerably by moderate ventilation. The lag of the thermometers nged from 3 to 72 seconds, whereas that of the barographs in still air ranged om 22 to 64 minutes. The lag of the temperature element of the meteorograph as found to be 3 minutes in still air and 11 seconds in an air stream of 17 miles er hour.

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I. INTRODUCTION

The thermometric lag of aircraft thermometers used to measure air temperatures may introduce considerable error when the instruments are used under conditions where the air temperature is changing. Such conditions exist, for example, during the climb of an aircraft or a sounding balloon, and here the lag of the air thermometer must be considered if accurate measurements are desired.

Determinations have been made of a constant, which is called the time lag, for a representative group of indicating and recording instruments which were selected from those available from time to time during the past five years. A number of the temperature elements, including experimental types, of the electric resistance thermometers which were constructed for the National Advisory Committee for Aeronautics and the Bureau of Aeronautics of the United States Navy have also been tested. The cooperation of these organizations,

of the Weather Bureau, and of the various manufacturers who s
mitted instruments for the investigation is acknowledged.

Owing to their value to the designer of instruments and perhaps
others, data have also been obtained on a number of thermomet
of types not ordinarily used in aircraft.

In addition, measurements of this constant have been made
representative types of barographs. The data obtained are of partic
lar value in computing the thermal lag of barographs during th
test in the laboratory for the effect of temperature, and thus furnis
ing in a measure the minimum time required for the instrument
come to any chosen degree of temperature equilibrium in the temp
ature chamber. Further, when no provision is made for the measu
ment of the instrument temperature either in flight tests or in hi
altitude flights, the approximate temperature of the instrument m
be computed from a knowledge of the time lag, together with data
the ventilation of the instrument during flight and the air temperatu
at the ground level. This temperature is useful in estimating
determining the error introduced by the variation of the temperatu
of the barograph.

II. RELATION OF TIME LAG AND THERMOMETRIC LA

A detailed discussion of the question of thermometric lag is giv
in a paper by Harper.[1] The method, apparatus, and procedure a
described in a previous paper.[2] With some modifications this
repeated here for ready reference.

In general, a problem of thermometric lag can be treated wi
sufficient accuracy by assuming that Newton's law of cooling appli
that is, that the rate of change in the temperature of the thermomet
is proportional to the difference between this temperature and th
of the surrounding medium. If T be the temperature of the thermom
eter or instrument, t the time, and U the temperature of the mediu
Newton's law is expressed by the equation—

$$\frac{dT}{dt}=\frac{1}{\lambda}(U-T) \tag{1}$$

where λ is a constant which will be called the time lag, since it ha
the dimensions of time.

The equation is written so as to make λ a positive constant, fo
if λ is positive, and U is higher than T, dT/dt will also be positive
The constant of proportionality is written in the form $1/\lambda$ for con
venience, because when so written λ can be interpreted in a simpl
and useful manner.

Two cases differing as to the temperature, U, of the bath or sur
rounding medium are of interest here. In the first case the tem
perature has a constant value U_0, that is—

$$U=U_0 \tag{2}$$

In the second, the temperature varies uniformly with time at a rat
r, that is—

$$U=U_0+rt \tag{3}$$

[1] Thermometric Lag, B. S. Bull., **8**, p. 659–714; 1912. (S. 185.)
[2] H. B. Henrickson and W. G. Brombacher, Lag of Thermometers and Thermographs for Aircraft
Mo. Weather Rev., **55**, p. 72–73; 1927.

Integrating equation (1) on the basis of the assumption expressed equation (2) gives the relation—

$$\log_e \frac{T_0 - U_0}{T - U_0} = \frac{t}{\lambda} \tag{4}$$

this equation U_0 is the temperature of the bath or medium in hich the thermometer or instrument is placed, T_0 the initial tem- rature of the thermometer at time $t=0$, and T the temperature of e thermometer, at time t.

If on the other hand, the temperature of the bath is changing in e manner defined in equation (3), the integration of equation (1) es the expression—

$$T - U = -r\lambda + (T_0 - U_0 + r\lambda)\, e^{-\frac{t}{\lambda}} \tag{5}$$

hen t, the time in which the instrument has been in the bath, large compared with λ, the time lag, the last term of the right- nd member of equation (5) becomes negligible. This condition the most common one. Equation (5) then reduces to—

$$T - U = -r\lambda \tag{6}$$

equations (5) and (6), U_0 and T_0 are the initial temperatures, at me $t=0$, of the bath and the thermometer, respectively; U and are the corresponding temperatures at time t; r is the rate of ange of temperature of the bath; and e is the base of natural garithms (2.72).

It follows from equation (4), that if a thermometer be plunged to a bath maintained at a constant temperature (the thermometer ing initially at a different temperature), λ is the number of seconds which the difference between the thermometer reading and the ath temperature is reduced to e^{-1} times its initial value.

The time required to reduce the difference in temperature between he thermometer and the bath to any fractional amount of the original ifference can be easily computed from equation (4). The computa- on shows that the difference in temperature reduces to 0.1, 0.02, nd 0.01 of its original value in a time of 2.3λ, 3.9λ, and 4.6λ, spectively. For example, if a thermometer having a time lag of 0 seconds under the conditions of use is initially at a temperature f +20° C. and is then placed in a bath at −30° C., it will indicate -25° C. in 23 seconds, −29° C. in 39 seconds, and −29.5° C. in 46 econds.

As a further example which is of some practical interest in testing struments, assume an instrument to have a lag of 20 minutes in ill air, and to be initially at a temperature of +20° C. If it is ut into a test chamber held constant at a temperature of −30° ., the air in the chamber being at rest, the instrument temperature ill drop to −25° C. in 2.3×20 or 46 minutes, and to −29° C. in 8 minutes, or 1.3 hours.

For the conditions under which equation (6) applies, the following nterpretation obtains:

If a thermometer has been immersed for a long time in a bath hose temperature is rising at uniform rate, λ is the number of econds between the time when the bath attains any given tempera-

ture and the time when the thermometer indicates this temperatur
In other words, it is the number of seconds the thermometer "lags
behind such a temperature.

As is evident from equation (6), the difference between the tem
perature of the bath and the thermometer, is the product of th
time lag and the rate at which the temperature of the medium
bath is changing.

The thermometric lag is of especial importance in the measureme
of air temperature during the climb of an aircraft. In the performan
testing of aircraft a maximum rate of climb is usually maintaine
and, therefore, the temperature of the free air in the vicinity of th
aircraft is decreasing. Although the rate of decrease of temperatu
is by no means constant owing to the falling off in the rate of clim
with altitude and the possible existence of inversions in the air tem
perature gradient, the order of magnitude of the difference in tempe
ature between the thermometer and the air can be evaluated
equation (6). It may be assumed that the time lag of a thermomet
increases as the density of the air decreases or as the altitude increas
which in some measure offsets the effect due to the falling off in rat
of-climb with altitude. With these reservations in mind, assum
that an airplane climbs at a rate of 3,000 feet per minute in an atmo
phere in which the average conditions of free air temperature exis
The value of r is then approximately 0.1° C. per second. Furth
assume that the time lag, λ, of the thermometer when exposed to th
free air moving at the air speed of the airplane is 10 seconds. Insertin
these values in equation (6) it is seen that $(T-U)$ equals 1° C., whi
means that the indication of the thermometer lags 1° C. behind th
free air temperature. If the time lag is assumed to be 30 seconds, th
indication lags 3° C.

The indications of instruments are affected by changes in temper
ture. This fact is of particular importance in the case of barograph
used in the measurement of air pressure at high altitudes. Th
approximate temperature of the instrument must be known in orde
to determine the pressure accurately. Since the time lag, λ, is rel
tively large for barographs, equation (5) applies, and not the simpl
equation (6). A computation shows that if T_0 is equal to U_0, th
temperature differences given by equations (5) and (6) are the sam
within 2 per cent when t exceeds 4 λ. As an example, assume that
barograph has a time lag of 20 minutes under the conditions of u
and that the temperature of the surrounding air decreases by 3°
per minute. The temperature differences on these assumption
determined by both equations (5) and (6) are given in Table 1.

TABLE 1

Time (minutes)	Air temperature U	Barograph temperature T	Temperature difference $(T-U)$	
			Equation (5)	Equation (6)
	° C.	° C.	° C.	° C.
0	20	20	0	
1	17	20	3	
5	5	19	14	
10	−10	14	24	
20	−40	−4	36	
30	−70	−23	47	

It is recognized that the temperatures to which a barograph may be subjected during flight do not follow the simple assumption of a uniform rate of decrease. In fact, actual conditions are such that a substantially uniform decrease of temperature is experienced during the first part of a climb, followed by a period during which the temperature of the surrounding air is practically constant. Such cases can be dealt with by application of both formulas (4) and (5).

II. METHOD OF DETERMINING LAG AND EXPERIMENTAL PROCEDURE

Equation (4) was adopted as the basis for the method of determining the time lag λ, of the thermometers and barographs. For this purpose, the equation is written in the form

$$\lambda = \frac{t}{\log_e \frac{T_0 - U_0}{T - U_0}} \tag{4a}$$

in which the notation is the same as that previously given.

The temperature elements of the thermometers under test were brought to a temperature $T_0 = 0°$ C. by packing them in ice, and the barographs and meteorograph to $T_0 = -20°$ C. by placing them in a cold chamber. Thin sheet metal containers, just large enough to hold the various thermometer bulbs, were used to keep the bulbs dry while packed in cracked ice. Each instrument was then suddenly immersed in the air stream of a wind tunnel at room temperature U_0, which was approximately $+25°$ C. Observations were made of the changing readings of the thermometers at known intervals of time. The temperature of the air in the wind tunnel, U_0, was also noted and was found to be constant during the short period of time required to obtain the wind-tunnel observations, usually about one minute. In the case of the barograph tests this time was decidedly longer, but the change in room temperature was always found to be negligible. Any inaccuracies in this connection would result in marked deviations from a straight line of the points at the right ends of such curves as are plotted in Figures 1 or 2.

The wind tunnel consisted of a cardboard tube 10 inches in diameter built around two electric fans, one placed at each end of the tunnel. An opening was cut in the middle of the tube and a Pitot-Venturi nozzle of known calibration was inserted in order to measure the air speed. The pressures developed by the nozzle were observed on a water manometer. On 110 volts the fans developed an air speed of 30 miles per hour; and on 220 volts, an air speed of 17 miles per hour. The bulbs of all indicating instruments were placed in the wind tunnel so that the long axis of each instrument or element was at right angles to the axis of the wind tunnel. The principal planes of the temperature elements of the thermographs were parallel to the axis of the wind tunnel during the tests. In the case of the Ferguson meteorograph, the air channel of the instrument was placed at an angle of approximately 45° with the axis of the wind tunnel. All barographs were tested with their covers in place and with their long axes parallel to that of the wind tunnel.

IV. RESULTS OF TESTS ON THERMOMETERS AND THERMOGRAPHS

The time t, plotted against the ratio

$$\frac{T_0 - U_0}{T - U_0}$$

is shown in Figures 1 and 2 for representative instruments. The ratio is plotted on a logarithmic scale using common logarithms. The slope of the line is the time lag, λ, provided that the abscissas are converted to logarithms to the base e. A brief description

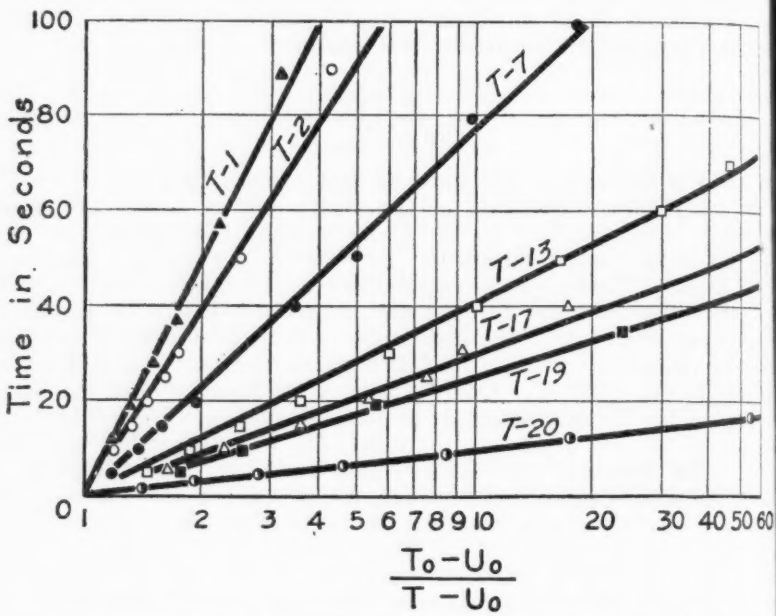

FIGURE 1.—*Data on thermometers and thermographs in an air stream of 17 miles per hour*

The time in seconds required for the instrument to attain a temperature of T° C. is shown as a function of the quantity

$$\frac{T_0 - U_0}{T - U_0}$$

where T_0 is the initial temperature of the instrument and U_0 the temperature of the medium in ° C.

the instruments, including values determined for the lag, is given below. Sketches of representative thermometer bulbs are given in Figures 3 and 7, and their lags in an air stream of 17 miles per hour are given in tabular form in the summary, the bulbs being arranged in the order of decreasing lag values.

Data given by Harper for a "chemical" mercurial thermometer cover a range from 0 to about 24 miles per hour. Extension to flying speeds involves a very considerable extrapolation, but by plotting $1/\lambda$ against the logarithm of the speed the curve can be approximately rectified. Extrapolation of this rectified curve indicates that at flying speeds the lags of all the thermometers described

below would be reduced to approximately one-half of those determined at the air speed of 17 miles per hour. The data for two air speeds given for instruments T–15 and T–22 in the following, also indicate that at flying speeds the lag would be about one-half of that determined at 17 miles per hour.

The thermometers tested may be conveniently divided into the following types: Liquid-filled, vapor-pressure, liquid-in-glass, bimetal, and electric-resistance. Of these the liquid-filled, vapor-pressure and electric-resistance types may be used for distant indication.

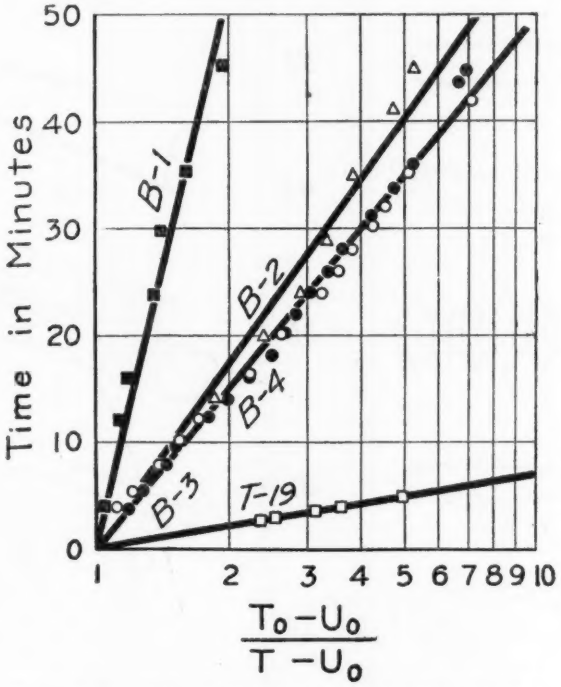

FIGURE 2.—*Data on barographs and a meteorograph in still air*

The time in minutes required for the instrument to attain a temperature of T° C. is shown as a function of the quantity $\frac{T_0-U_0}{T-U_0}$ where T_0 is the initial temperature of the instrument and U_0 the temperature of the medium in °C.

It is obvious that the time lag of an instrument of any given type depends largely upon the design of that particular instrument. Thus for the liquid-in-glass instruments, the time lags given below range from 17 to 57 seconds in an air stream of 17 miles per hour. The design in turn must meet the service requirements, the effect of which is illustrated by the difference in the time lags of the liquid-in-glass strut and laboratory thermometers. The lags range from 32 to 57 seconds for the strut type, and from 17 to 28 seconds for the laboratory type. However, allowing for the differences in time lag of individual designs of a given type of thermometer, each type is inherently limited in the lowest value which may be obtained. Thus

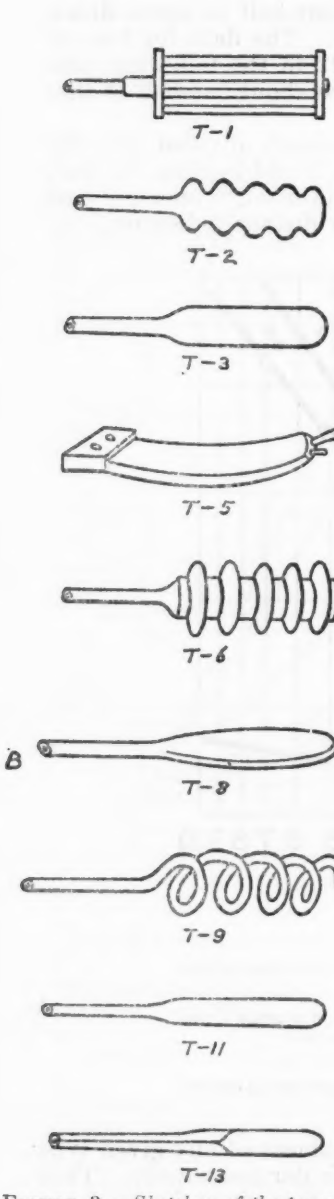

FIGURE 3.—*Sketches of the temperature elements of a number of thermometers and thermographs*

T-1, liquid-in-metal tubes; T-2, liquid-in-glass strut thermometer bulb; T-3, liquid-in-glass strut thermometer bulb; T-5, liquid-filled bourdon tube; T-6, liquid-in-metal bulb; T-8, liquid-in-glass strut thermometer bulb; T-9, liquid-in-metalcoil; T-11, liquid-in-glass thermometer bulb; T-13, liquid-in-glass thermometer bulb.

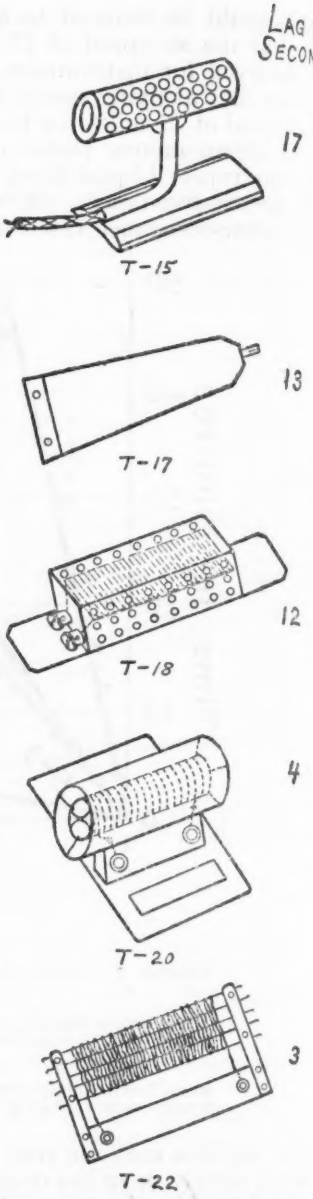

FIGURE 7.—*Sketches of various typ of temperature elements for electri resistance thermometers and of a t metal element*

T-15, electric resistance element, three lay No. 36 nickel wire; T-17, bi-metal strip eleme 0.023 inch thick; T-18, electric resistance eleme two layers No. 36 nickel wire; T-20, electric sistance element, one layer No. 40 nickel wi T-22, wire weave resistance element, one la No. 40 nickel wire.

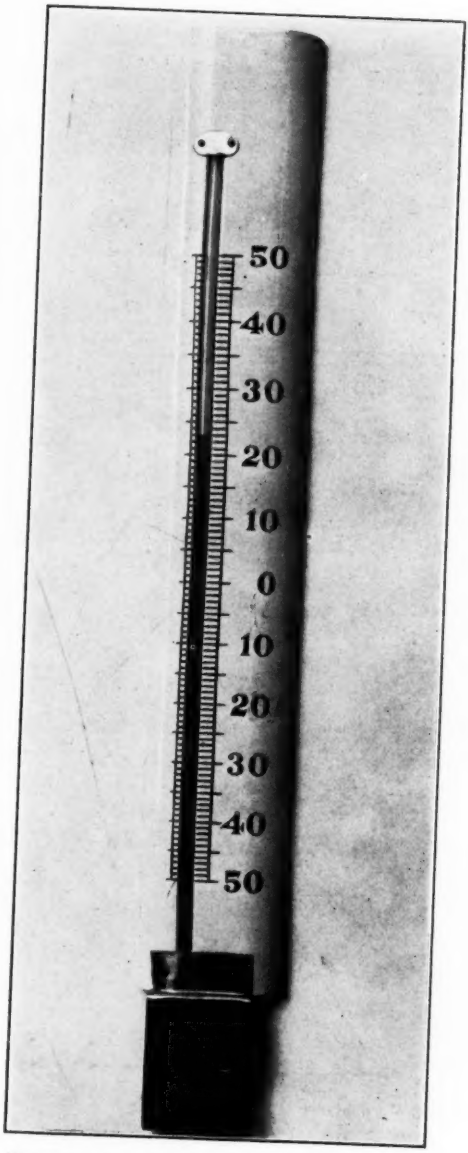

FIGURE 4.—*Airplane strut thermometer for measuring free air temperature*

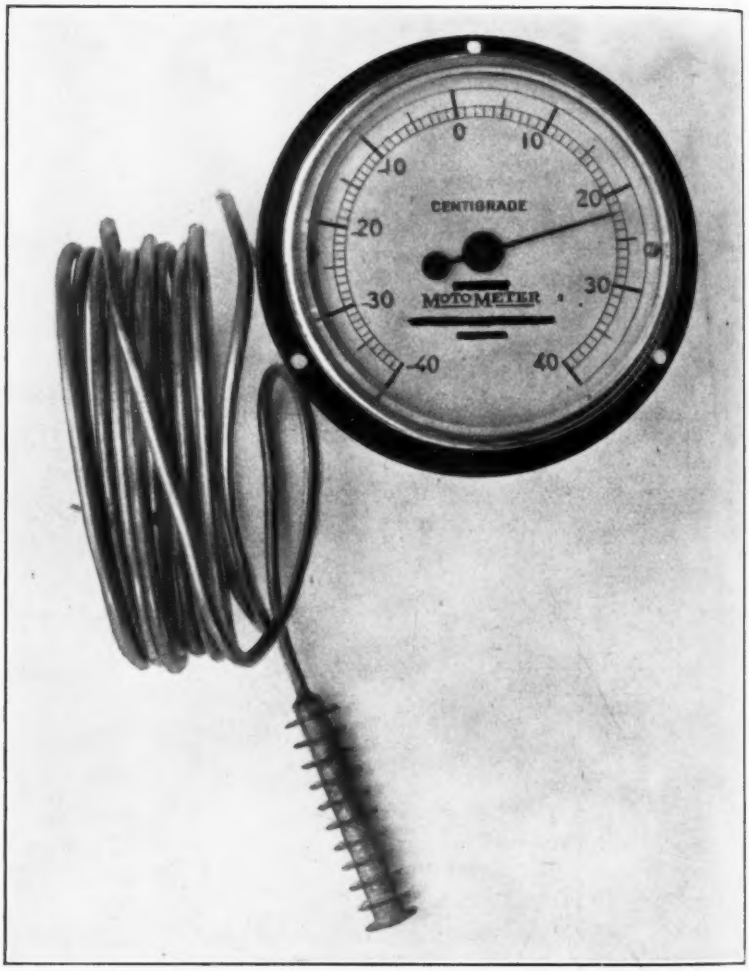

FIGURE 5.—*Liquid-filled, distant indicating aircraft thermometer*

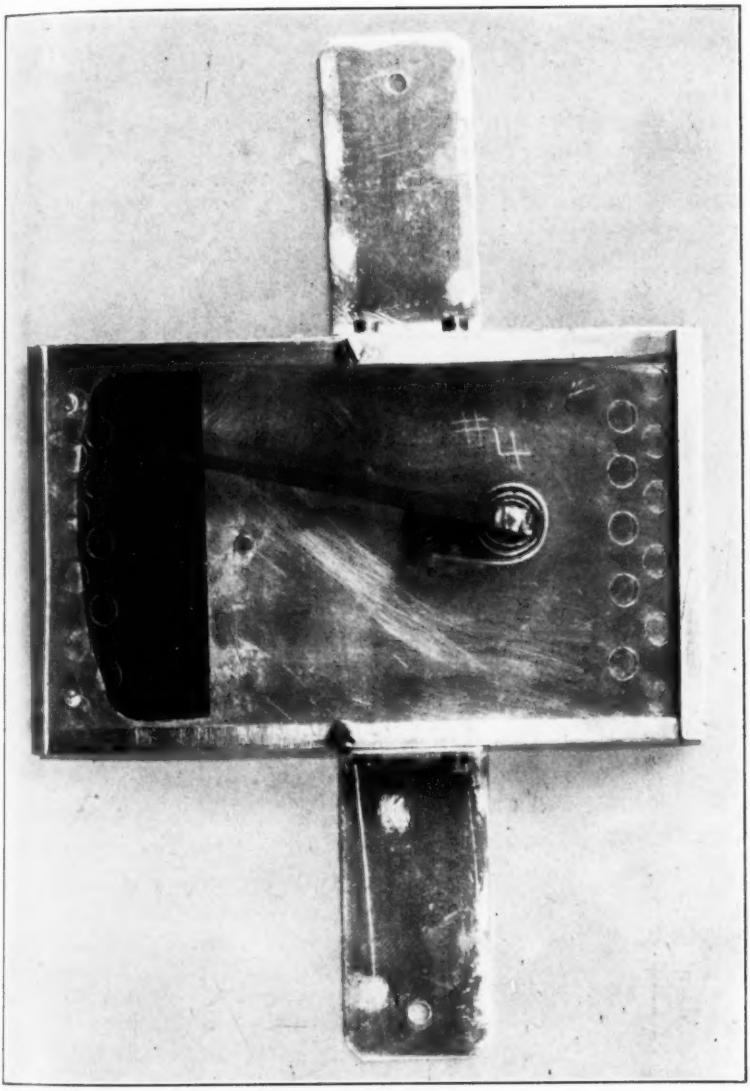

FIGURE 6.—*Minimum temperature recording strut thermometer*

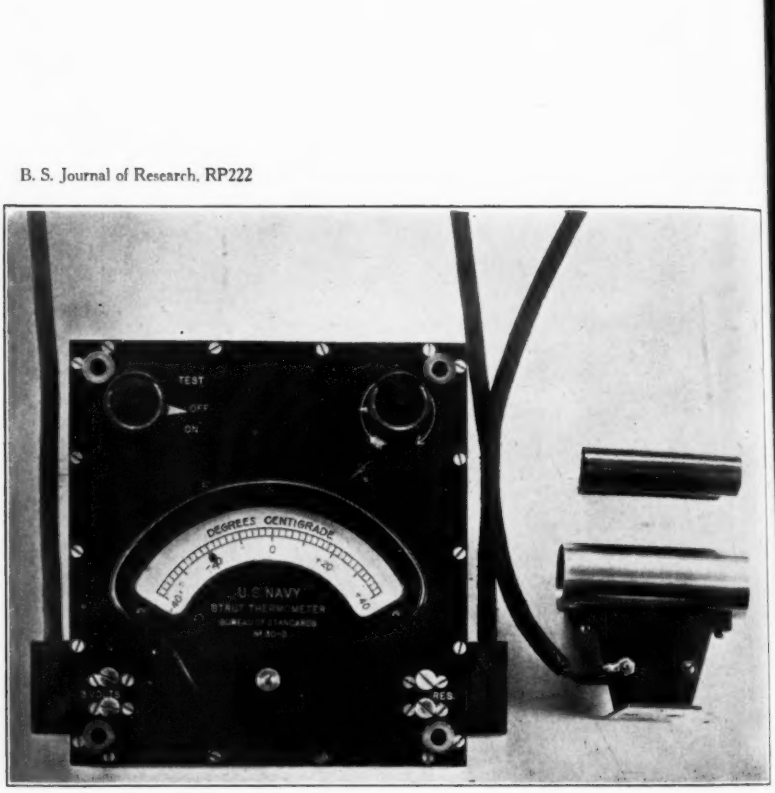

FIGURE 8.—*Electric resistance thermometer for measuring free air temperature*

The temperature element is shown to the right, and above it the resistance coil.

the data show that a thermograph with a bimetal element can be made with a lower lag than one with a liquid-filled Bourdon tube. In general, the time lag of properly designed liquid-filled elements of all types usually exceeds that of bimetal elements which in turn exceeds that of comparable resistance elements. It is realized that other factors enter into the choice of a type to be used so that the final decision is usually a compromise.

The time lags given in the following list are those for exposure in an air stream of 17 miles per hour unless otherwise noted.

T–1. Thermograph with liquid-in-metal-tubes bulb.—This instrument was originally designed to record free air temperature. The bulb was to be mounted on the strut and the recorder in the cockpit. The instrument also contained an element for recording the air temperature in the cockpit, the lag of which is reported under T–5. The tubular bulb, consisting of five metal tubes arranged in the form of a gridiron, was unusually large. Each tube measured 7 inches in length by 0.19 inch in external diameter. In addition to having a considerable mass of liquid, the element also had a considerable mass of metal. The bulb is represented in sketch T–1 of Figure 3. Time lag, λ, 72 seconds.

T–2. Strut thermometer, liquid-in-glass bulb.—This is a column-type instrument such as is shown in Figure 4 and is designed for use as an airplane strut thermometer. The corrugated cylindrical bulb of this instrument was unusually large compared with the ordinary chemical thermometer, and contained a considerable mass of glass and liquid. It measured 1.75 inches in length by 0.43 inch in diameter. It was protected by a metal sun shield which was perforated at the leading and trailing ends so as to permit air-flow around the bulb. The over-all dimensions of the entire thermometer were 26.5 inches in length, by 3.75 inches in width, by 1 inch in thickness. The bulb itself was like that shown in sketch T–2 of Figure 3. Lag, 57 seconds.

T–3. Strut thermometer, liquid-in-glass bulb.—This instrument was of the same make as T–2, but of slightly different bulb design, as may be seen by comparing sketches T–2 and T–3 of Figure 3. The bulb was 2 inches long, and of circular cross section measuring 0.31 inch in diameter. This bulb also contained a considerable mass of liquid. Lag, 52 seconds.

T–4. Radiator thermometer, vapor-pressure type.—This type of instrument is commonly used to measure the temperature of the cooling water or oil of an airplane motor. The instrument had a metal bulb 3.5 inches long, with a circular cross section measuring 0.44 inch in diameter. Lag, 48 seconds.

T–5. Thermograph, Bourdon tube liquid-filled.—This unit was the part of the instrument described under T–1 which measures the air temperature in the cockpit. The Bourdon tube was 2.5 inches long, 1.25 inches wide, and 0.12 inch thick. A sketch of the element is shown in T–5 of Figure 3. Lag, 46 seconds.

T–6. Strut thermometer, distant reading, liquid-filled.—This instrument had a liquid-filled bulb with 11 radiation disks placed along its length. The bulb was 3.1 inches long, and had a circular cross section which measured 0.4 inch in diameter. The outside diameter of the radiation disks was 0.75 inch. The bulb is shown in sketch

T–6 of Figure 3. A photograph of the entire instrument is shown in Figure 5. Lag, 39 seconds.

T–7. Thermograph, Bourdon tube, liquid-filled.—The Bourdon tube was 2.25 inches long, 0.62 inch wide, and 0.06 inch thick. The temperature element was similar to that shown in sketch T–5 of Figure 3. The over-all dimensions of the instrument were 6.5 inches in length, by 8 inches in height, by 3.75 inches in width. Lag, 33 seconds.

T–8. Strut thermometer, liquid-in-glass.—This instrument was somewhat similar to T–3 described above, including also the cover for protecting the bulb from the sun. The instrument differed from T–3 in that the bulb was much better streamlined and had less mass. Instead of a circular cross section, the bulb had a very flat elliptical cross section with the narrow edge heading into the air stream. The length of the bulb was 3.25 inches, the width 0.50 inch, and the thickness 0.19 inch. A sketch of it is shown in T–8 of Figure 3. Front and profile views of the instrument are shown in Figure 4. Lag, 32 seconds.

T–9. Strut thermometer, liquid-in-metal helical bulb.—This instrument was of the same general type as T–6 described above, except that the bulb in this case was made in the form of a long tubular helix of approximately five turns. The over-all length of the coiled bulb was 5.5 inches, and the diameter of the tube was 0.44 inch. The bulb of this instrument is shown in the sketch T–9 of Figure 3. Lag, 30 seconds.

T–10. Minimum-temperature-recording strut thermometer.—This instrument was designed primarily for recording the minimum temperature of the free air at the ceiling of high altitude flights. A bimetallic strip of brass and invar-steel, with a thickness of 0.030 inch and a width of 0.25 inch, coiled into a flat spiral of two and one-half turns, was securely attached to an aluminum base plate which could be taped to the strut. A rectangular piece of celluloid, bent over a streamlined form, served as a cover that had the advantage of being transparent. The leading and trailing edges of this cover were perforated in order to allow the air stream to ventilate effectively the temperature element. The weight of the entire instrument was 2 ounces. A photograph of the device is shown in Figure 6. Lag, 29 seconds.

The same bimetal coil with pointer attached was removed from its casing, and mounted on a thin flat piece of bakelite 0.06 inch thick, by 2.5 inches wide, by 4.25 inches long. Without covering of any kind, the coil was placed in the wind tunnel in such a position that the air stream could readily flow through its convolutions. The lag, when determined in this manner in an air stream of 17 miles per hour, was found to be reduced to 10 seconds.

T–11. Laboratory thermometer, liquid-in-glass type.—The bulb of this thermometer was cylindrical in shape, 0.75 inch in length by 0.22 inch in diameter. The over-all length was 12 inches. The liquid was believed to be colored pentane. This bulb is shown in sketch T–11 of Figure 3. Lag, 28 seconds.

T–12. Laboratory thermometer, liquid-in-glass type.—The bulb of the thermometer was clyindrical in shape, 1.25 inches in length by 0.25 inch in diameter. The thermometer had an over-all length of 12 inches, and was very similar to T–11. Lag, 26 seconds.

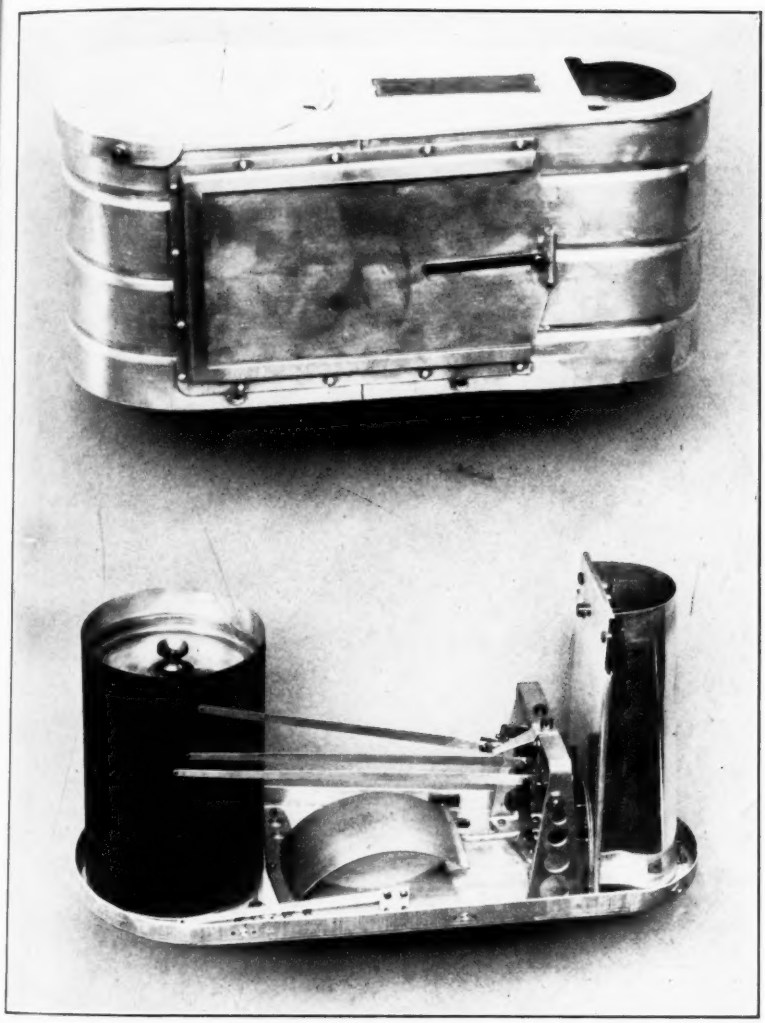

FIGURE 9.—*Fergusson meteorograph*

The bimetallic temperature element is mounted in the channel at the right end of the instrument.

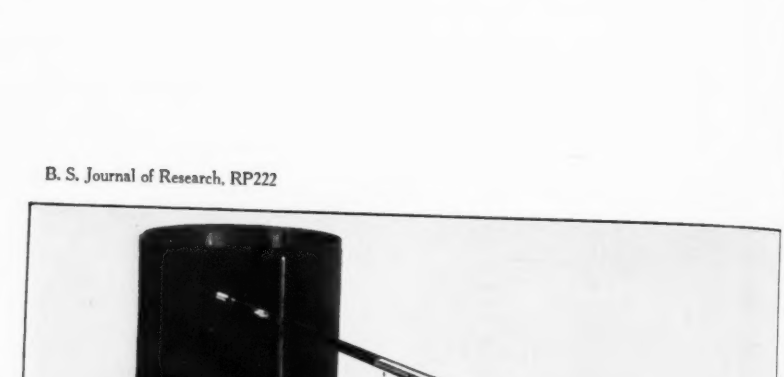

FIGURE 10.—*Dual traverse barograph with cover removed*

The lower stylus records the instrument temperature.

T–13. Laboratory thermometer, mercury-in-glass type.—The bulb was cylindrical in shape, 0.5 inch in length by 0.19 inch in diameter. The instrument had an over-all length of 10 inches. As the thermometer was filled with mercury, the lag was somewhat less than for a similar instrument filled with a liquid such as pentane. The bulb of the instrument is shown in sketch T–13 of Figure 3. Lag, 18 seconds.

T–14. Laboratory thermometer, mercury-in-glass type.—The bulb of this thermometer was very similar to T–13. It was cylindrical in shape, 0.63 inch in length by 0.19 inch in diameter. The instrument had an over-all length of 9 inches. Lag, 17 seconds.

T–15. Electric resistance thermometer, model No. 1.—This instrument was constructed for the National Advisory Committee for Aeronautics by the Bureau of Standards. T–15 was the first of a series of experimental types of resistance elements which were constructed. It is shown in the sketch T–15 of Figure 7. The element consisted of a three-layer coil of No. 36 single silk-covered nickel wire, wound on a thin, hollow, metallic bobbin 2.25 inches long by 0.62 inch in diameter. The resistance was 205 ohms at +20° C. Holes were bored into the outside protecting tubing so as to reduce the thermal lag. For this particular element the lag was found to be 17 seconds (the average of six determinations) in an air stream of 17 miles per hour. The lag was found to be 22 seconds (the average of two determinations) in an air stream of 10 miles per hour.

T–16. Thermograph, flat bimetallic strip temperature element.—This instrument was designed and built by the Bureau of Standards for the Bureau of Aeronautics, Navy Department, for the purpose of recording free-air temperatures in flight test work. The invar-brass bimetal temperature element was very similar to that shown in the sketch T–17 of Figure 7. It measured 2.75 inches long, 1 inch wide at the fixed base of the strip tapering to 0.75 inch at the end, and 0.030 inch thick. The strip was insulated from the aluminum base of the thermograph by mounting it upon a block of bakelite. Lag, 15 seconds.

T–17. Thermograph, bimetallic strip temperature element.—The thermal element of this recording instrument of foreign make was very similar to T–16 described above. The flat strip, 2.5 inches long by 1 inch wide by 0.023 inch thick, is shown in the sketch T–17 of Figure 7. Lag, 13 seconds.

T–18. Electric resistance thermometer, model No. 2.—This element was designed and constructed for the National Advisory Committee for Aeronautics. The temperature element consisted of No. 40 single silk covered nickel wire, wound around a rectangular piece of brass, 0.093 inch thick by 2.56 inches long by 0.87 inch wide, of which the inner portion was removed so as to leave an eighth of an inch margin all around. The nickel wire, 200 ohms at 26° C., was secured to the brass frame with bakelite varnish. This frame was then mounted within a perforated housing of 0.09 inch brass, 1.12 inches wide by 2.56 inches long, in order to give it mechanical support and protection from the sun. The over-all length including the projecting ends of the base of the box was 7.75 inches. The projecting ends afford a ready means for attaching the element to the airplane. The sides of the protective casing were perforated with many holes in order to secure adequate ventilation of the inclosed temperature element.

The element in its housing is shown in sketch T–18 in Figure 7. Lag, 12 seconds.

T–19. Thermograph of Fergusson meteorograph.—This meteorograph was of the type used by the Weather Bureau in sounding balloons for the purpose of obtaining temperature, pressure, and humidity data of the upper atmosphere. It is shown in Figure 9. It was made almost entirely of aluminum sheeting about 0.008 inch in thickness. The weight of the entire instrument was 7 ounces and the over-all dimensions, 8.25 inches in length, 3.5 inches in height, and 3.37 inches in the greatest width. The temperature element was of phosphor-bronze, invar-steel bimetal and was made in the form of a three-fourths closed collar, 1 inch wide, 0.62 inch in diameter, and 0.012 inch thick. The element was mounted in a channel open at both ends with the axes of the element and the channel concentric. The fixed end of the element was attached to an insulating block of bakelite, 1 inch long by 0.31 inch square.

When testing the instrument in the wind tunnel, the axis of the air channel was at an angle of approximately 45° with respect to that of the tunnel. When testing for lag in still air, the air channel was in the vertical position and both ends were kept uncovered and free from obstruction. The time lag was 11 and 20 seconds, when the air stream in the wind tunnel was 17 and 10 miles per hour, respectively. In still air the lag was three minutes.

T–20. Electric resistance thermometer, model No. 3.—This design of the temperature element for the electric resistance thermometer (with minor modifications) was found to be the most satisfactory, and is the type with which the instruments constructed by the Bureau of Standards for the National Advisory Committee for Aeronautics and Bureau of Aeronautics of the Navy Department were finally equipped. In this design a decided reduction in lag was obtained. A No. 40 single silk covered nickel wire was wound in a single layer around a thin copper cylinder that was equipped with internal, length-wise, radiation fins. This copper shell was only 0.002 inch in thickness. In addition to their function of radiating heat, the internal fins also served to strengthen the cylinder. The cylinder measured 0.50 inch in diameter by 2 inches in length. The nickel wire, 200 ohms at −20° C., was fastened to the cylinder with bakelite varnish which has a comparatively high thermal conductivity. The temperature element was protected from the direct rays of the sun as well as from mechanical injury by inserting it lengthwise and concentric within a piece of fairly heavy-walled brass tubing which measured 0.75 inch in diameter and 2.25 inches in length. The temperature element unit was supported within the protective tubing by means of three thin metal strips spaced 120° apart at each end of the tube. This construction is illustrated in sketch T–20 of Figure 7. A photograph of the entire instrument with slightly modified design of temperature element, but of substantially the same time lag as T–20 is shown in Figure 8. Lag, four seconds.

T–22. Resistance temperature element.—An experimental temperature element consisting of nickel wire woven over seven parallel cotton strands was mounted on a light brass frame so as to be easily handled during tests. This is shown in T–22 of Figure 7. The wire was No. 40 single silk covered nickel, 200 ohms at +20° C., woven into a rectangular mat 2.75 inches long by 0.62 inch wide. This mat

was mounted in the wind tunnel with its length parallel to that of the tunnel. Tests on the element made with and without a coating of bakelite varnish resulted in the same lag. Tests were made in air streams of 10 and 17 miles per hour speeds giving lags of four and three seconds, respectively.

V. RESULTS OF TESTS ON BAROGRAPHS

The results of the time lag determinations on five typical barographs, made in a manner somewhat similar to the tests on the thermometers and thermographs, are given in the following paragraphs. In each case the tests were made with the instrument covers in place, which is the service condition. The lag was determined first in still air, and then in air moving with a speed of 10 miles per hour. Barographs in service receive little or no ventilation. Tests in the 10 miles per hour air stream were made in order to ascertain the effects of a moderate amount of ventilation. A coiled bimetal temperature indicator, similar to T–10 described above, was installed successively on each barograph tested. This coil was securely fastened to the metal base-plate, as close as possible to the pressure element. The lag of thermometer bulbs is usually expressed in seconds, whereas the lag of barographs is more conveniently expressed in minutes. A plot, similar to that in Figure 1 which shows the time lag results for thermometers, is given in Figure 2 for the barographs.

B–1. Common barograph, wooden case.—This barograph had a mahogany casing 0.31 inch thick, covering a wooden base which was somewhat thicker. The recording drum and pressure capsules were mounted on a heavy brass base 0.09 inch thick, by 3.75 inches long, by 3 inches wide. The over-all dimensions of the wooden casing were 7 inches in length, by 5 inches in height, by 4.37 inches in width. A glass cover, 5.75 inches long by 3 inches wide, occupied most of the front side of the case. The total weight was 3 pounds and 4 ounces. Lag in still air, 74 minutes. Lag in an air stream of 10 miles per hour, 14 minutes.

B–2. Common barograph, aluminum case.—This barograph had an aluminum casing 0.31 inch thick. The recording drum and pressure capsules were mounted on an aluminum base plate 0.08 inch thick, by 4.75 inches long, by 3 inches wide. This plate was mounted upon four small bushings so that there was a quarter of an inch clearance between it and the bottom of the case. The over-all dimensions of the aluminum casing were 6.5 inches in length, by 4.5 inches in height, by 4 inches in width. A full-sized celluloid window was fitted into the front side of the instrument. The weight of the barograph was 1 pound and 5 ounces. Lag in still air, 25 minutes. Lag in an air stream of 10 miles per hour, 9.5 minutes.

B–3. Dual-traverse barograph.—This dual-traverse barograph was of the type commonly used in high altitude flights and in flight test work. The instrument with the cover removed is shown in Figure 10. This view also shows the coiled bimetal temperature indicator used in making the lag tests. The barograph was made entirely of metal, with a heavy aluminum base and a painted sheet copper casing. The over-all dimensions were 8.5 inches in length, by 7.5 inches in height, by 4.5 inches in width. The total weight was 5

pounds and 2 ounces. Lag in still air, 22 minutes. Lag in an air stream of 10 miles per hour, 5 minutes.

B–4. Single-traverse barograph.—This barograph was of the same make and general case construction as the above instrument. The size and weight, however, were just about one-half those of the dual-traverse instrument. The over-all dimensions were 8 inches in length, by 5 inches in height, by 3.75 inches in width. The weight was about 3 pounds. Lag in still air, 22 minutes. Lag in an air stream of 10 miles per hour, 5 minutes.

VI. SUMMARY

1. THERMOMETERS, THERMOGRAPHS, AND METEOROGRAPH

The time lag of 22 temperature elements of thermometers and thermographs when ventilated by an air stream of 17 miles per hour has been determined. The results are given in the following list which is arranged in the order of decreasing values of the lag:

Instrument	Time lag (in seconds)
T–1. Thermograph, liquid-in-metal tubes	72
T–2. Strut thermometer, liquid-in-glass bulb	57
T–3. Do	53
T–4. Radiator thermometer, vapor-pressure type	48
T–5. Thermograph, Bourdon tube, liquid-filled	46
T–6. Strut thermometer, distant reading, liquid-filled	39
T–7. Thermograph, Bourdon tube, liquid-filled	33
T–8. Strut thermometer, liquid-in-glass	32
T–9. Strut thermometer, liquid-in-metal helical tube	30
T–10. Minimum-temperature-recording strut thermometer	29
T–11. Laboratory thermometer, liquid-in-glass	28
T–12. Do	26
T–13. Laboratory thermometer, mercury-in-glass	18
T–14. Do	17
T–15. Electric resistance thermometer, model No. 1	17
T–16. Thermograph, flat bimetallic strip temperature element	15
T–17. Thermograph, bimetallic strip temperature element	13
T–18. Electric resistance thermometer, model No. 2	12
T–19. Thermograph of Fergusson meteorograph	11
T–20. Electric resistance thermometer, model No. 3	4
T–22. Wire-weave electric resistance temperature element	3

In still air the lag of thermograph T–19 was three minutes.

2. BAROGRAPHS

The time lag of four typical aircraft barographs has been determined in still air as well as in an air stream of 10 miles per hour. The results, again listed in the order of decreasing lag values, are given in the following table.

Instrument	Time lag—	
	In still air	In air at 10 m. p. h.
	Minutes	*Minutes*
B-1. Common barograph, wooden case	74	14
B-2. Common barograph, aluminum case	25	9.5
B-3. Dual-traverse barograph	22	5.0
B-4. Single-traverse barograph	22	5.0

In general, the metal cased barographs have considerably less thermal lag than the wooden cased instruments. Moderate ventilation, such as in an air stream of 10 miles per hour, reduces the lag by approximately one-fourth.

WASHINGTON, June 7, 1930.

APPARATUS FOR THE DETERMINATION ABOARD SHIP OF THE SALINITY OF SEA WATER BY THE ELECTRICAL CONDUCTIVITY METHOD

By Frank Wenner, Edward H. Smith, and Floyd M. Soule[1]

ABSTRACT

The apparatus described furnishes a convenient means for the determination of the salinity of samples of sea water as they may be collected. It consists essentially of a Wheatstone bridge, conductivity cells of a type which may be filled and emptied during fairly rough weather, and the necessary auxiliary equipment, all built into a single cabinet.

A special feature is the use of two similar conductivity cells in adjacent arms of the bridge. When both are filled with samples of sea water, even though not of the same salinity, both have very nearly the same temperature coefficient, so the balance of the bridge is not greatly affected by small uncertainties of the temperature. Further, the complicated actions taking place at the electrodes, generally referred to as polarization, are substantially the same in both cells, so the effects of polarization are largely neutralized.

A further special feature, not really a part of the equipment but of a plan for its use, is that a supply of standard sea water or sea water of which the salinity has been determined by laboratory methods is carried aboard and used for periodic standardizations. Samples of sea water to be tested, together with a sample of standard sea water, are substituted one after another in the same conductivity cell. This gives a direct comparison of the sample of unknown salinity with that of a standard, almost if not quite independent of the cell constant, largely independent of other constants of the equipment and largely independent of systematic errors.

Apparatus of the type has been used during the past several seasons in the International Ice Patrol Service, also on the *Marion* expedition and on the last cruise of the nonmagnetic vessel *Carnegie*.

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I. INTRODUCTION

No doubt the idea of determining the salinity of sea water from measurements of its electrical conductivity has occurred to many. Some of the attempts made during the years 1914 to 1921, inclusive, to perfect apparatus for this purpose are described in Bulletin No. 9

[1] Frank Wenner, National Bureau of Standards; Edward H. Smith, United States Coast Guard; and Floyd M. Soule, Carnegie Institution of Washington.

of the United States Coast Guard entitled "Ice Observations and Ice Patrol Service for the Season 1921." Much of this earlier work was done by A. L. Thuras, a part while he was connected with the National Bureau of Standards and a part while he was scientific observer in the Ice Patrol Service.

To give satisfactory results the apparatus should be capable of reproducing measurements of the electrical conductivity to 1 part in 4,000, corresponding roughly to changes of 10 mg per liter total salt and something less than 1 part in 100,000 in the density. This could be obtained readily in the laboratory, but the conditions at sea are such as to make the problem much more difficult. For convenience in use, the equipment should be relatively small in size and constitute a unit rather than an assemblage of a number of pieces of apparatus. Further, it should be capable of being operated from the lighting circuit of the ship on which it is installed. The equipment must be sufficiently rugged or so protected as not to suffer mechanical injury during the severest storms, and should be capable of being used during rough weather. The electrical insulation must remain good in the presence of an ocean atmosphere, and should not be injured in case sea water is spilled over parts of the apparatus. As the temperature coefficient of the electrical conductivity of sea water is in the neighborhood of 2 or 3 per cent per ° C. to obtain a precision of 1 part in 4,000 the temperature must be controlled to better than one-hundredth ° C. or provision made to compensate for uncertainties of the temperature. Also the various manipulations necessary in making measurements should be the simplest possible consistent with obtaining the precision sought.

The first apparatus intended to fill these requirements was designed by Wenner in 1922, and constructed in the Bureau of Standards during the latter part of 1922 and the early part of 1923. The original calibration was based on measured constants of the apparatus and the data concerning the electrical conductivity of sea water obtained in the earlier investigations referred to above. This apparatus was installed in the United States Coast Guard cutter *Tampa* just before the beginning of the 1923 International Ice Patrol Service, when the first attempts to use it were made by Smith, then scientific observer. Between the 1923 and 1924 ice-patrol seasons Smith made a rather complete calibration of the instrument using titrated samples of sea water. A description intended primarily for the information of those whose duty it might be to use the apparatus is given in Bulletin No. 12 of the United States Coast Guard, entitled "International Ice Observations and Ice Patrol Service Season 1924." Since then two additional equipments have been constructed, one on contract for the Coast Guard, which will be referred to as the second equipment, and one by the Department of Terrestrial Magnetism of the Carnegie Institution of Washington, which will be referred to as the third equipment, or the Carnegie Institution equipment. Since the second equipment for the Coast Guard was completed both the first and second have been used in the Ice Patrol Service, excepting the past two seasons when only one was available, the other having been destroyed by fire while in storage between seasons. Also one equipment was used on the *Marion* expedition into Baffin Bay during the summer of 1928. Some reference to the results obtained in the use of the first two equipments will be found in re-

ports of the Coast Guard since 1924. The third equipment was installed on the nonmagnetic vessel *Carnegie* just prior to her departure on her Cruise VII. This equipment was used by Soule from the time of its installation in the spring of 1928 until the fall of 1929 when the cruise was terminated by the destruction of the vessel. Some idea of the performance of this equipment will be given in this paper, although the complete data collected will be published by the Carnegie Institution of Washington, along with the other results of the expedition, in the reports of the *Carnegie's* Cruise VII.

The reader must bear in mind that two of the three instruments built have been destroyed by fire and that the third is not at present available to the authors. Consequently this paper has been prepared from notes, laboratory data, photographs, field records, and memory. Therefore, there occur in the following pages, statements which are general where the authors would have preferred to give specific

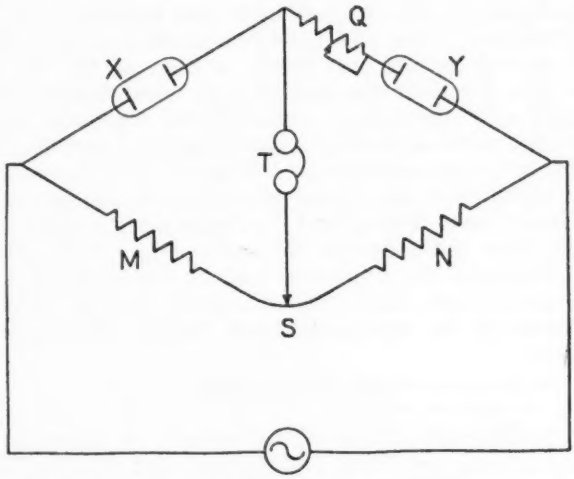


FIGURE 1.—*Simplified diagram of electrical circuit*

quantitative data. It is believed, however, that the lack of such specific data will neither keep the theory from being understood nor be a serious disadvantage in the design and construction of other such instruments.

II. METHOD OF MEASUREMENT

A simplified diagram of the electrical circuit is shown in Figure 1. Here X and Y represent two similar electrolytic cells, and also the resistance of these cells when filled with sea water. Q is an adjustable resistance in series with Y. M and N are fixed resistances, S is a slide wire, $\sim$ represents the source of the alternating test current, and T is the telephone receiver for indicating a lack of balance of the bridge. A special feature is the use of two similar cells in adjacent arms of the bridge. When both cells are filled with sea water, even though the salinity of the sea water in one is not the same as that in the other, both have very nearly the same temperature-

coefficient. If, therefore, Q is small in comparison with Y, the differential temperature coefficient between X and $(Y+Q)$ will be small in comparison with that of the electrical conductivity temperature coefficient of the sea water in the X cell. As a consequence, the balance of the bridge is not greatly affected by small uncertainties of the temperature, provided both cells are very accurately at the same temperature. As in all bridge measurements the precision obtainable is limited among other factors by the heating produced by the test current. However, with this arrangement the test current raises the temperature of the sea water in both cells above that of the bath, in which the cells are located, by substantially the same amount since the thermal characteristics of the two cells are closely alike. Consequently a much larger test current may be used than would otherwise be permissible. Further, the complicated actions taking place at the electrodes, generally referred to as electrolytic polarization, will be substantially the same in both cells, so that the effects of polarization in one cell upon the balance of the bridge is largely neutralized by the effects of polarization in the other cell.

Another special feature not really a part of the bridges but a part of the plan for their use and kept in mind during the design is that a supply of Copenhagen standard sea water or sea water of known salinity or known density is carried aboard and used in periodic standardization of the equipment. Samples of the sea water to be tested, and samples of the standard sea water or sea water whose properties have been determined by laboratory methods, are substituted one after the other in the same cell. This gives a direct comparison between the unknown and standard samples almost if not quite independent of the cell constant, largely independent of other constants of the equipment, and largely independent of systematic errors.

III. CIRCUITS

A complete diagram of the bridge circuit is shown in Figure 2. Here W and P are two fixed resistances with the equivalent of a slide wire between them, and together they constitute the Wagner branch with the contact connected to the inclosing metallic shield G. The Wagner branch serves to bring the telephone receivers to the potential of the shield to which the observer is connected, and so forms a part during measurements. The switch or key R serves to connect one of the detector (telephone receiver) terminals of the bridge to the shield and this disturbs the balance of the bridge except when the Wagner branch is properly adjusted. This key is closed only during this adjustment. L is a mutual inductance between one of the leads from the source of the test current and the telephone leads. It serves to introduce into the telephone circuit a quadrature electromotive force so as to balance any of the out of phase components of potential difference in the bridge from whatever source they may arise, such as capacitance to ground, capacitance in the cells, polarization, etc. This mutual inductance is adjustable from a small negative through zero to a small positive value. To balance the bridge requires a proper setting of the slide wire contact or index, a proper setting of the mutual inductance, and a proper setting of the contact on the Wagner branch. As these three adjustments are not independent of each other, they must, in principle at least, be

made in successive approximations. However, if the slide wire first is set at a point giving a minimum sound in the telephones and this sound then reduced as much as possible first by an adjustment of the mutual inductance and then by an adjustment of the Wagner branch, these two adjustments usually will be sufficiently exact, so that the slide wire contact may then be adjusted with the required precision. Only in case the reading of the slide wire index corresponding to the second adjustment differs materially from that of the first, need additional adjustments of the mutual inductance or the Wagner branch be made. There is nothing to be gained by repeating either unless a third adjustment of the slide wire contact is made. The reading of the slide wire index for the adjustment made

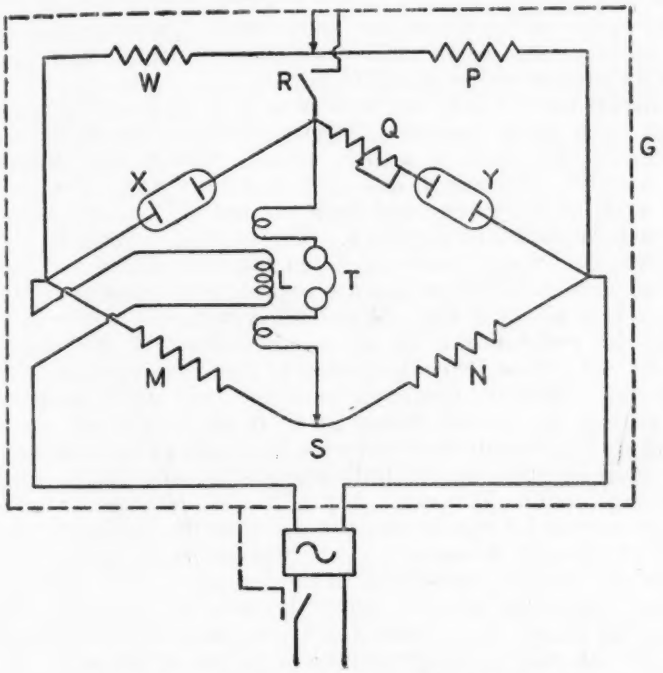


FIGURE 2.—*Complete diagram of bridge circuit*

after the adjustments of the mutual inductance and the Wagner branch is the only one which is significant. However, the final adjustment of the contact on the slide wire should not be made until a sufficient time after placing a sample of sea water in the X cell for the establishment of temperature equilibrium to well within 0.01° C.

IV. COAST GUARD EQUIPMENT

1. DESCRIPTION

A photograph of the second equipment is shown in Figure 3. Here the doors of the cabinet are removed to give an unobstructed view of the various parts. It will be seen that there are four compartments. The lower compartment on the right contains the bath in which the main part of two X and one Y cells, a thermoregulator,

a stirring propeller, and heating units are located. The upper compe ment on the right contains the stirring motor, relay, air circulat fan, upper parts of the cells, thermoregulator heaters, the conn tions between the cells and the rest of the measuring circuit, and lamp for keeping the compartment dry. The lower left compartme contains a microphone hummer for producing the alternating c current. This is packed in hair felt to prevent sound from it int fering with the detection of sound of the same pitch in the telepho receivers. The upper left compartment contains the major part the measuring circuit, a lamp for keeping the compartment dry, t various switches and key, and the telephone receivers when not use. Both upper compartments are metal lined except at their to and the arrangement is such that sea water, spilled in either can get into either of the lower compartments. These linings and t metal walls of the bath are electrically connected and constitu the major portion of the shield *G*.

Conditions aboard ship are such as to make it impracticable to u an open bath or to handle cells except during favorable weath consequently, the bath is tightly closed, though not hermetica sealed, and the cells are so designed that they may be emptied a refilled without being removed from the bath. A photograph of o of the cells is shown in Figure 4. The central portion of the cell approximately 10 cm long and 1 cm internal diameter. The e bulbs containing the electrodes are approximately spherical and ha a diameter of about 3 cm. When filled with sea water of averag salinity, the resistance is in the neighborhood of 200 ohms. T electrodes are hollow truncated cones of platinum covered with pla num black. They are arranged so as to avoid undue concentrati of the current in the sea water at their edges, and so as to avo trapping air bubbles on their surface. From each electrode a platinu wire extends through an end bulb into a side tube which extends u ward along the side of the cell. A quantity of mercury in each of the side tubes serves for connecting the cell into the bridge circuit. Th cell is filled through the small funnel at the top and emptied by siphon ing through the tube connected to the bottom of the lower termina bulb and extending upward along the side of the cell. The cel are mounted in metal supports which terminate at their upper end i a ring, and this ring is clamped to the metal top of the bath. A rubbe gasket between the ring and the top of the bath serves to make water-tight connection. Inside this ring is a metal tube about 6 cm in diameter and about 6 cm long. This tube is filled with wax, whic constitutes the main part of the fastening between the cell and it metal support. The wax also serves for closing the bath so that sea water can not be spilled into it and to better insulate the cell from the metal shield.

The slide wire is of the Kohlrausch type having 10 turns and a resistance from 25 to 30 ohms. The exact value is not of much impor tance, and further can not conveniently be made to have an even valu such, for example, as 25 ohms. The range of the slide-wire inde extends from zero to 1,000 divisions and the wire within this range or as much of it as will be used, should be fairly uniform. The slid wires used were made by the Leeds & Northrup Co., of Philadelphia The resistance of the end coils *M* and *N* are made equal and of such magnitude that their combined resistance plus the resistance of the

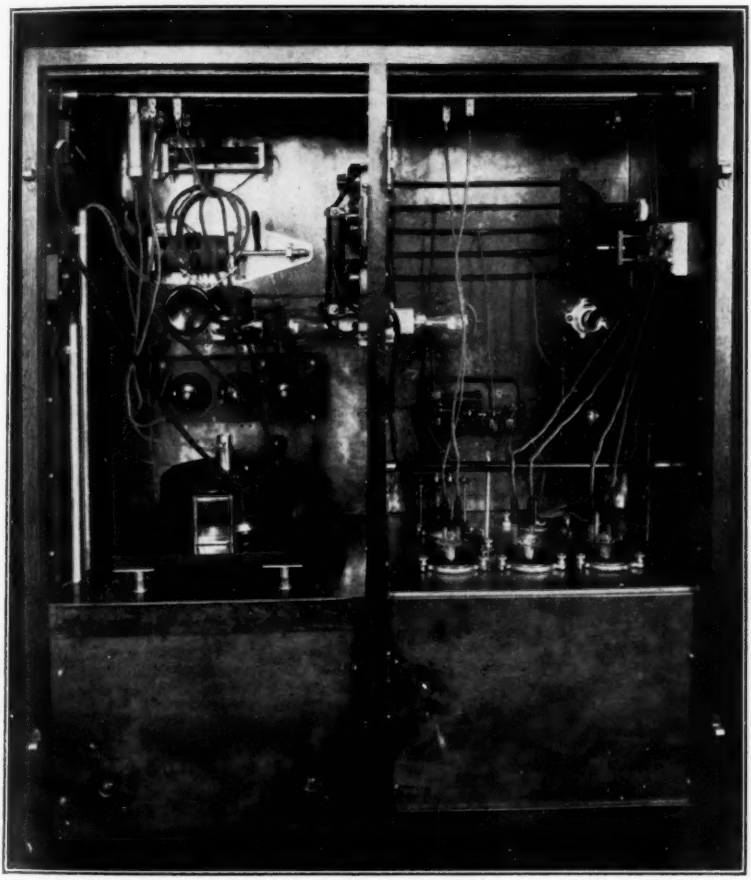


FIGURE 3.—*Second instrument for United States Coast Guard*

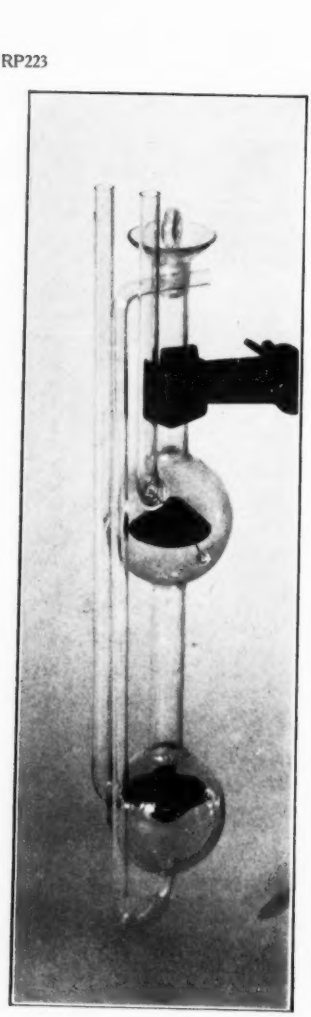


FIGURE 4.—*Unmounted electrolytic cell*

slide wire is accurately 15,000 times the resistance per division of the slide wire as measured by the graduations of the head or frame which carries the contact. The end coils are metal covered, except at their lower end, and preferably hermetically sealed. Further, they are mounted in the upper part of the cabinet so there is little chance of sea water being spilled upon them, and little chance that they will be injured if such spilling occurs. The resistance of each of the fixed coils of the Wagner branch is in the neighborhood of 200 ohms, and that of the slide wire between them is about 40 ohms. Each telephone receiver has a resistance of about 10 ohms and a probable impedance at 1,000 cycles of the order of 100 ohms. The resistance Q is adjustable over a range of about 5 ohms in steps as small or smaller than 0.05 ohm. The contacts in Q have indices, so that after a change it can be reset to a former value.

The test current has a frequency of 1,000 cycles per second and is supplied by a microphone hummer made by the General Radio Co., of Cambridge, Mass. For the operation of this hummer a 6-volt

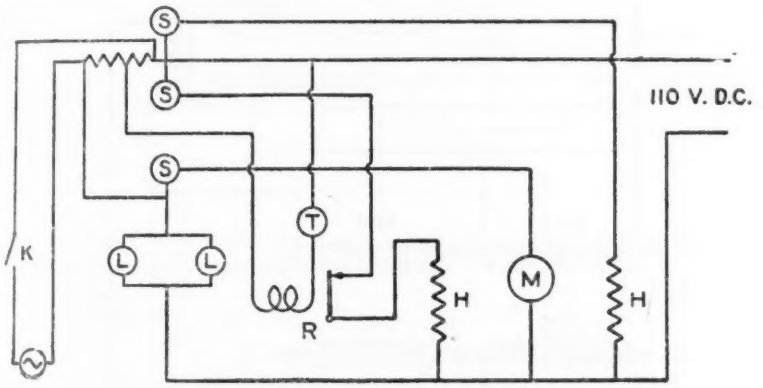


FIGURE 5.—*Diagram of power circuit*

direct-current source is required, also for the operation of a relay used in controlling the temperature 2 to 4 volts is required. To get these 2 low direct-current voltages from the direct current lighting circuit of from 100 to 120 volts, taps are made across a resistance connected in series with two lamps in parallel, each of about 50 watts. One of these lamps is located in each of the two upper compartments and serves to keep the inside of the cabinet at a temperature above the surrounding air. This elevated temperature is, or may be, of material assistance in maintaining the insulation of the measuring circuit. The lighting circuit of the ship also furnishes power for driving the motor which stirs the bath in which the cells are located, and for maintaining the bath at the desired temperature. A diagram of the power circuit is shown in Figure 5. Here S, S, S, represents switches; M, the motor for stirring the bath; H, H, heaters for keeping the bath at the desired temperature; T, thermoregulator; R, relay with armature contact in series with one of the bath heaters; L, L, lamps, one in each compartment, for keeping the upper compartments dry and substantially at the same temperature as the bath; and K is a switch or key in the power circuit to the hummer.

A diagram of the hummer circuit is shown in Figure 6. It should be noted that the hummer circuit is such that the measuring circuit is insulated from the circuit supplying power to the hummer; that is, the lighting circuit of the ship. At this point it should be mentioned that the key in the circuit supplying power to the hummer is of the spring type, normally open, and so arranged with respect to a small metal plate connected to the shield that when the key is held closed by the observer he almost of necessity is connected to and thus constitutes a part of the shield as stated above. The connections between the parts of the bridge circuit in the two upper compartments are made by horizontal metal tubes in the top of the cabinet, and these are well insulated. Also, other parts of the bridge circuit are arranged with a view of keeping the insulation high. Each winding of the mutual inductance between one of the leads supplying the test current and the telephone leads consists of approximately 50

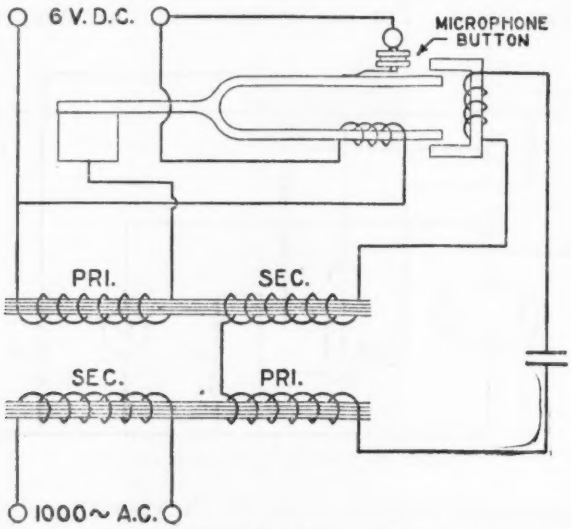


FIGURE 6.—*Diagram of microphone hummer circuit*

turns of insulated wire on tubes which telescope into each other. One of these windings is in two parts, one in each of the telephone leads, and these windings are differentially connected so that by sliding one tube with respect to the other the value of the mutual inductance can be changed continuously from a negative to a positive value. Between these two windings is the third winding, one end of which is connected to and thus forms part of the shield.

2. CALIBRATION

It can be shown that a second-degree equation should give a good approximation to the calibration curve for this type of instrument.

Consider the conditions where a solution of known salinity S' and of resistivity R' is placed in the cell X. Let X' be the resistance of the arm of the bridge including the cell X and let N and M be the resistances of the ratio arms with the slide wire set to some reading s' which corresponds to the salinity S' and let the bridge be balanced by

adjusting the resistance Q. Then if $(Q+Y)$ represents the resistance of the arm including Q we can write

$$X' = (M/N)\ (Q+Y) \tag{1}$$

If now the sea water in the measuring cell is replaced by a sample of higher salinity S and consequently lower resistivity R' and the bridge is balanced by increasing the slide-wire reading from s' to s, the resistance of the arm containing the measuring cell is given by the equation

$$X = \frac{M\ (1-m\ (s-s'))}{N\ (1+n\ (s-s'))}(Q+Y) \tag{2}$$

where m is the resistance of one division of the slide wire divided by M, and n is the resistance of one division of the slide wire divided by N. From equations (1) and (2) we have

$$X = X' \frac{(1-m\ (s-s'))}{(1+n\ (s-s'))} \tag{3}$$

Since the same cell has been used for the two samples, the ratio of resistivities of the two samples is the same as the ratio of the resistances, and hence

$$R = R' \frac{(1-m\ (s-s'))}{(1+n\ (s-s'))} \tag{4}$$

If C and C' represent conductivities; that is, the reciprocals of R and R', respectively, equation (4) can be written

$$C = C'\ [1+(n+m)\ (s-s')+(mn+m^2)\ (s-s')^2+ (m^2n+m^3)\ (s-s')^3 \cdots] \tag{5}$$

The relation between electrical conductivity and salinity of sea water over the range 30 to 40 ‰ salinity can be closely approximated by the equation

$$C = C'\ (A+BS)$$

where A and B are constants and S is the salinity. Substituting this expression for C in equation (5) gives us

$$A+BS = 1+(n+m)\ (s-s')+(mn+m^2)\ (s-s')^2+ (m^2n+m^3)\ (s-s')^3 \cdots$$

or

$$S = \frac{1-A}{B}+\frac{(n+m)}{B}(s-s')+\frac{(mn+m^2)}{B}(s-s')^2+\frac{(m^2n+m^3)}{B}(s-s')^3 \cdots$$

which can be written

$$S = S'\left[1+\frac{(n+m)}{S'\ B}(s-s')+\frac{(mn+m^2)}{S'\ B}(s-s')^2+ \frac{(m^2n+m^3)}{S'\ B}(s-s')^3 \cdots\right] \tag{6}$$

where S' is the salinity corresponding to the conductivity C'.

From the work of E. Ruppin [2] and A. L. Thuras [3] mean values of the constants A and B give the relation that

$$C_s = C_{35}\ (0.10925 + 0.02545S)$$

where C_s is the conductivity at any salinity S ‰ and C_{35} is the conductivity at a salinity of 35 ‰ (‰ = parts per 1,000). With these values of A and B equation (6) can be written

$$S = 35\left[1 + \frac{(n+m)}{0.89075}(s-s') + \frac{(mn+m^2)}{0.89075}(s-s')^2 + \frac{(m^2n+m^3)}{0.89075}(s-s')^3 \cdots\right]$$

in which s' is the slide-wire reading corresponding to a salinity of 35 ‰. Inspection shows that, if, as was true of all the instruments so far built, one division of the slide wire represented 1/15,000 of the sum of the resistances of the ratio arms, all terms involving $(s-s')$ to exponents greater than 3 may be neglected, and that the third degree term need only be considered when $(s-s')$ is numerically large.

Among the laboratory tests which should be made on an instrument of this sort is the test for uniformity of the slide wire. Differently stated, the corrections to the slide-wire reading as an indication of the ratio of the resistances of the two arms should be determined. Thus, if the resistance of one division of the slide wire is to be 1/15,000 the total resistance of the two arms, a slide-wire reading of 750 should occur when the ratio of the resistance of N to the resistance $(N+M)$ is 7,750/15,000. If actual test shows the ratio to be 7,753/15,000, the correction to be applied to the slide-wire reading at 750 is 3. A table of such corrections should be determined, at least for that part of the slide wire which is to be used.

Having tested the slide wire for uniformity and quantitatively determined its irregularities, it is then possible to construct a calibration curve or table for converting slide-wire readings into values of salinity from published data on the conductivitiy of sea water. This, as in all methods of calibrating such an instrument, involves the arbitrary selection of one point on the calibration curve.

A more satisfactory method of arriving at the values for a table for converting slide-wire readings into salinities would be the selection of one point on the curve and the determination by measurement of two other points. This involves the use of three samples of known and different salinities. The curve could then be closely approximated by drawing the curve of a second-degree equation through the three known points. Such a method would have the advantage of eliminating uncertainties regarding conductivity relations and possible differences between theory and application. It would have the disadvantage of building upon the errors of individual determinations.

A third and even better method of calibration would be the actual measurement of a large number of samples of known salinity well distributed over the range of the instrument. This was the pro-

[2] O. Krümmel, Handbuch der Oceanographie, Band I, p. 291.
[3] A. L. Thuras, J. Acad. Sci., Washington, D. C., 8, p. 685; 1918.

cedure followed by Smith in the calibration of the first two instruments. The calibration of the first bridge, was made in this way during the winter of 1923–24 at the Museum of Comparative Zoölogy, of Harvard University, using about 70 samples whose salinities were determined by titration. These samples had been collected from the North Atlantic during the ice season of 1923, and consequently were particularly well suited for the calibration of this instrument, since they came from the same regions in which the bridge was to be used. In this calibration the range was so selected that a salinity of 35 $^0/_{00}$ corresponded to a slide-wire reading of 650.3. The resulting calibration curve can be expressed by the equation

$$S=35\ [1+293.4\times10^{-6}\ (s-650.3)+29.5\times10^{-9}\ (s-650.3)^2] \qquad (8)$$

In order to compare this equation with equation (7) let us put $s'=650.3$ whence it follows that $n=1/7{,}650.3$ and $m=1/7{,}349.7$. With these numerical values equation (7) becomes

$$S=35\ [1+299.5\times10^{-6}\ (s-650.3)+40.7\times10^{-9}\ (s-650.3)^2] \qquad (9)$$

The data on which the constant B (see equation (6)) is based involve differences of 0.0075 reciprocal ohm-cm and, therefore, the uncertainty in the coefficients of equation (9) is 1.3 per cent which means that the first-degree coefficient may be in error by as much as 4×10^{-6}. The difficulty of accurately evaluating the second-degree coefficient of an experimentally determined calibration curve is, in a measure, responsible for the poorer agreement of these coefficients in equations (8) and (9).

There is a further uncertainty arising from the fact that the bridge was out on ice-patrol service for one season after the initial slide-wire test before the calibration was made, and a second slide-wire test made after the second season showed that the lower turn of the slide wire had suffered some corrosion during the intervening two seasons. Bearing in mind the combined uncertainties, equations (8) and (9) show good agreement.

3. PROCEDURE IN USE

Before the apparatus can be used for the determination of the salinity of a number of samples of sea water, preliminary tests and adjustments must be made. These consist of putting into the Y cell a suitable sample of sea water and determining and recording the setting of Q for each of the X cells to be used.

First, all the cells to be used should be filled with sea water of the same, though not necessarily known salinity. Then with any one of the cells used as a Y cell, any other cell used as an X cell, and Q set at about the center of its range, a setting of the index of the slide wire is found at which the bridge is balanced. It should be remembered that in any case a balance of the bridge involves a proper setting of the mutual inductance and of the contact on the Wagner branch. This setting of Q should be recorded; then another cell is used as an X cell and the bridge balanced this time without changing the setting of the slide wire index, but by a change in the setting of Q. In like

manner, a setting of Q, which gives a balance of the bridge for each the remaining cells used as X cells, is determined and recorded. T serves merely to find the differences in the cell constants and wh one of the cells has the lowest resistance when all are filled with s water of the same salinity.

In case no more cells are available than it is expected will be us at any one time, that cell whose resistance differs most from the av age resistance of all may be selected for use as the Y cell, and of t remaining cells that one having the lowest resistance may be used an X cell in the selection of a sample of sea water of suitable salini for use in the Y cell. This X cell is then filled with a sample of s water of definitely known salinity. Assuming the calibration cur or a table giving the readings of the slide-wire index corresponding different salinities is available, the reading corresponding to t salinity of the sea water in the X cell is found and the slide-wire ind set accordingly. By a series of trials a sample of sea water is fou for use in the Y cell such that the setting at Q for a balance of t bridge is well toward the lower limit. This may require mix samples of different salinity or even dilution or concentrati Finally, with the index of the slide wire set to the reading corresp ing to the salinity of the sea water to be used as a standard, the cells are filled with the standard sea water and for each the bridge balanced by an accurate adjustment of Q. This gives readings of for each of the X cells and these must be recorded, since the readi of Q for any one cell must be duplicated whenever it is used in maki a measurement. Having the readings of Q which, with the sea wat which is in the Y cell, gives with each X cell a reading of the slide-wi index corresponding to that given by the calibration curve for t salinity of the standard, the apparatus should be in readiness for us in making measurements.

In making measurements—

1. Any sea water which may be in X cells is removed by siphoning
2. Each cell is rinsed with some of the sea water next to be teste in it and then filled with more of this sea water.
3. After the first sample to be tested has come to the temperatur of the bath (which usually is about 15 minutes), Q is set at the readi corresponding to the particular X cell, and the bridge accurate balanced by an adjustment of the slide-wire index following th procedure outlined above.
4. The reading of the slide-wire index and any record of the sampl which it is desired to keep are recorded.
5. The sea water is removed by siphoning, the cell rinsed, and fille with the sea water next to be tested in it.
6. Another X cell is connected into the bridge in place of the first and Q set at the reading corresponding to the particular X cell, a similar procedure being followed in making the balance, recordin results, emptying, rinsing, and refilling.
7. In like manner, the reading of the slide-wire index is found and recorded for the sample of sea water in each of the remaining X cells, if any.
8. After the second sample placed in the first X cell has come to the temperature of the bath, it may be measured in like manner, and so on until all the samples which may be on hand have been measured.

9. At any convenient time the readings of the slide-wire index may be converted into salinities by reference to the calibration curve or to a table equivalent to the calibration curve.

10. As the salinity of the sea water in the Y cell will change with evaporation and condensation, and as the constants of the cells will change with possible variations in the platinum black coating of the electrodes, the readings of Q should be checked at the beginning and at the end of each run with samples of standard sea water in each of the X cells.

Because of the very large temperature coefficient of electrical conductivity of sea water, it is important that the solutions in the Y and X cells have the same temperature to within a few thousandths of a degree centigrade when final adjustments for balancing the bridge are made. The previously mentioned feature of design of having two adjacent arms similar in temperature coefficient characteristics makes the actual temperature of relatively small importance, but this is true only where these two arms are subjected to the same temperature conditions. It is therefore necessary for the operator to allow a sufficient length of time for the sample to attain the temperature of the bath after it has been introduced into one of the cells, before measurements can be made with accuracy. Experiments with the first apparatus in 1923 by Smith and with the *Carnegie* instrument in 1928 by Soule indicate that unless the sample introduced is initially close to the temperature of the bath a period of 15 minutes should be allowed for temperature equilibrium to be established.

As the setting of the resistance Q is a measure of that part of the sea-water resistance whose temperature coefficient remains uncompensated, it will be seen that it is desirable that all cells used as X cells be sufficiently similar that the setting of Q for each may be made fairly small.

The accuracy of an individual measurement made with either of the Coast Guard instruments is estimated to be about the same as with titration. That is, the error is within about 0.02 ‰ salinity. However, in the opinion of those who have used both methods, the electrical conductivity apparatus has the advantage that regardless of the violence of the ship's motion the actual measurement is unaffected and the difficulties connected with the handling of liquids under such conditions are much reduced, being restricted to those involved in putting the samples into the cells.

V. CARNEGIE INSTITUTION EQUIPMENT

1. DESCRIPTION

The instrument installed on the *Carnegie* was similar in principle to the first two, but differed somewhat in structural details. A comparison of Figure 7 with Figure 3 will make clear some of these differences. In the *Carnegie* apparatus the electrical switches and controls were mounted on bakelite panels in the upper parts of the two sections. The central partition was retained for the protection of the electrical circuits on the one side in case of accidental spilling of sea water on the other side.

As in the earlier models, the microphone hummer was located in the lower compartment of the left-hand side and surrounded by sound deadening packing. The slide wire was mounted directly above the lower compartment containing the microphone hummer. Mounted

on or back of the left-hand panel were the coils and rheostat for the third arm, the auxiliary resistance Q, the ground switch, the variable coupler for inductive balancing, terminals for the telephone receiver and a 40-watt incandescent lamp for keeping the humidity low. The switch button for the microphone hummer was placed on the central partition.

On the right-hand panel were mounted the relay for the heater control, the relay rehostat, the stirring motor rheostat, the main supply switch and fuses, a second lamp for drying, and double-pole single-throw switches for the stirring motor, the thermostat, and each of the three X cells. The lower part of the right-hand section was occupied by the water bath, the cover for which served as mounting for the auxiliary cell, the three X cells, the stirring motor and the pump, the mercury thermometer, the thermostat, and the two heating elements. Three X cells were provided instead of the two as used on the earlier instruments in order to reduce the average time necessary for a measurement. The bath was stirred by a small centrifugal fan which was driven by the stirring motor through a disk drive. The thermostat was of a simple, commercially obtainable type having a large mercury well surmounted by a small capillary tube containing two electrical contacts of platinum. The heating elements were also of a type which could be easily purchased. They were of the flat immersion type having a maker's rating of 250 watts each on 110 volts. In order to reduce the rate of heating, the two elements were placed in series. A mounted cell, two thermoregulators, one with and one without its cover removed, and a heating element are shown in Figure 8.

For purposes of electric shielding, the interior of the bridge was copper lined. This shield lining, and other exposed metal parts were nickel plated to better resist corrosion.

2. CALIBRATION

The time available for the calibration of the *Carnegie* apparatus prior to the departure of the vessel was limited, and, as the calibration of the slide wire as given by the manufacturer showed it to be very uniform, it was accepted without further test as to uniformity. From the experience of the Coast Guard cutters on ice-patrol duty it had been recommended that the calibration be so selected that the mid-point of the slide wire would correspond to a salinity of about 33.00 ‰. With this recommendation in mind, a rough calculation indicated that the Copenhagen standard water of 34.99 ‰ salinity should correspond to a slide-wire reading of 698.5. This was, therefore, selected as the first and invariable point on the calibration curve. With this point selected as being on the curve by definition, five other samples of known salinity furnished by the Scripps Institution of Oceanography and also titrated by H. R. Seiwell were alternately put into the X cells and the corresponding slide-wire readings determined. From these six well-distributed points a curve was drawn. This gave the data from which was constructed the initial calibration curve which was used to determine the salinity of unknown samples in terms of the Copenhagen standard sea water. From time to time as the cruise progressed some of the samples which were measured in the bridge were also titrated against standard sea water in a Knudsen burette by the silver-nitrate method. Each of these samples furnished

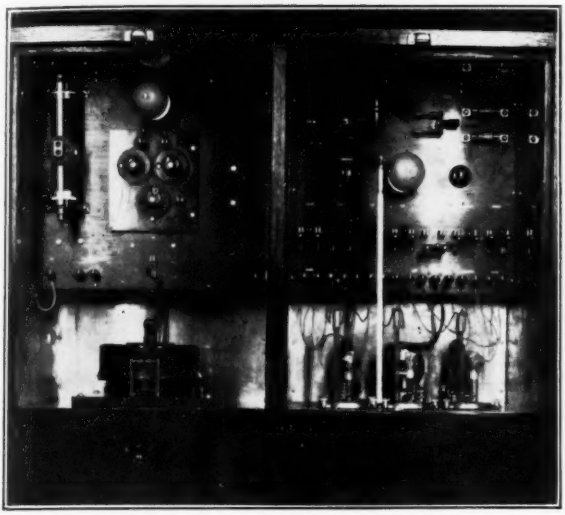


FIGURE 7.—*Carnegie equipment*

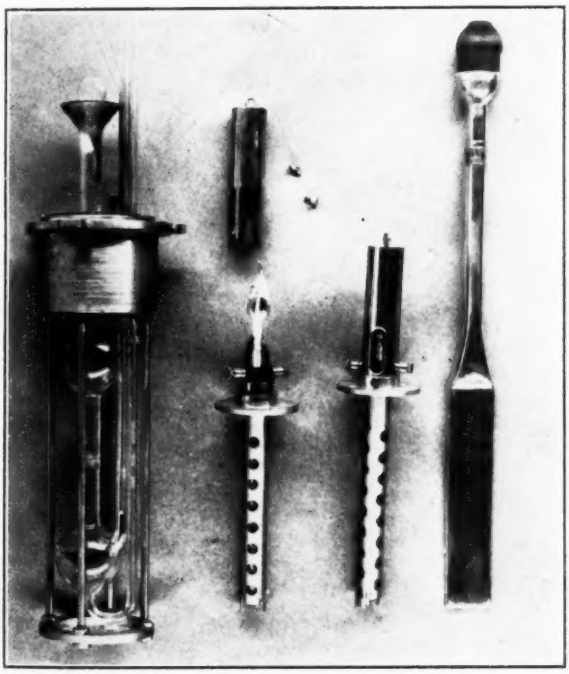
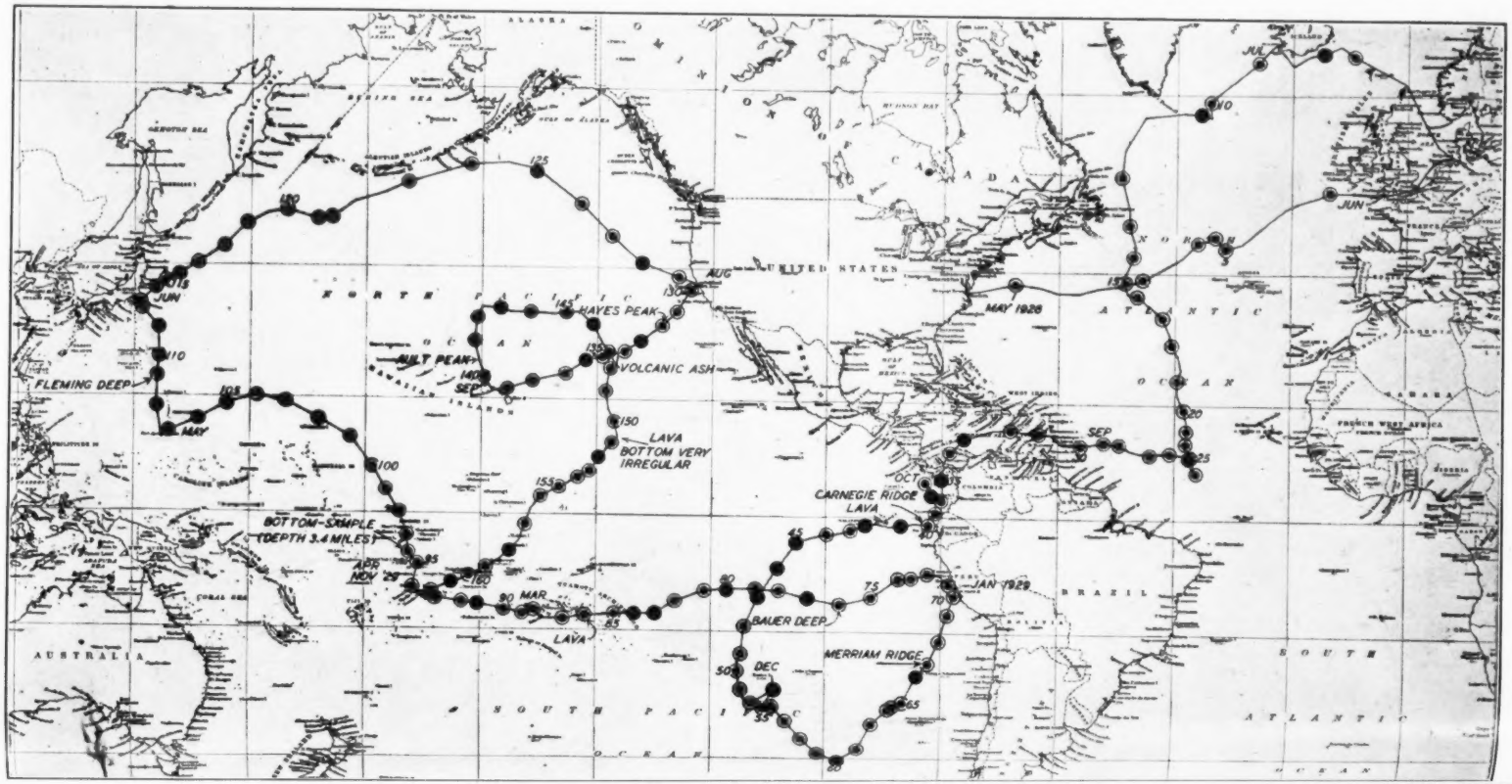


FIGURE 8.—*Mounted electrolytic cell, two thermoregulators one with cover removed, and heating element*


ALASKA
BERING SEA
GULF OF ALASKA
UNITED STATES
CANADA
HUDSON BAY
NORTH PACIFIC OCEAN
HAWAIIAN ISLANDS
HAYES PEAK
VOLCANIC ASH
AULT PEAK
FLEMING DEEP
LAVA
BOTTOM VERY IRREGULAR
BOTTOM SAMPLE (DEPTH 3.4 MILES)
CARNEGIE RIDGE LAVA
BAUER DEEP
MERRIAM RIDGE
MAY 1928
JAN 1929
AUSTRALIA
BRAZIL
SOUTH PACIFIC OCEAN
SOUTH ATLANTIC OCEAN
NORTH ATLANTIC OCEAN
FRENCH WEST AFRICA
JUN
JUL
AUG
SEP
OCT
NOV
DEC
MAR
APR
MAY

an additional point on the calibration curve. In all 220 such points, including the arbitrarily selected point, were determined and all used in determining the final calibration curve. Of these, 149 were determined at a temperature of 30° C. and 70 at a temperature of 40° C. Of the points determined at 30° C., 137 were true sea water samples and 12 were prepared or evaporated samples. Of the points determined at 40° C., 68 were true sea water samples and two were prepared samples. The true sea water samples were obtained at 35 different localities widely separated in geographical position, having a latitude range of about 104° from 63° 30′ north to 40° 24′ south and having a longitude range of about 201° from 14° 41′ west to 144° 01′ east. The geographical distribution is shown on the chart in Figure 9. The samples used for calibration comparisons were collected at stations indicated by the large dots, the small dots within the circles indicating the stations at which samples were measured but not checked by titration. The points cover a range of depth from the surface down to about 4,000 m. The vertical distribution is shown in Figure 10.

As an individual bridge measurement is accurate to about 0.01 to 0.02 ‰ salinity and as an individual titration measurement is also accurate to about 0.01 to 0.02 ‰, the combined instrumental and observational errors should lead to a scattering of the points of 0.04 ‰ on each side of the curve, representing the relation between salinities and slide-wire index readings. However, as the salinity bridge measures total salt as found, and the titration method measures total halogen salt as found and is corrected for other salt on the assumption that a fixed ratio of salt exists, it was expected that in some localities a considerably greater scatter than 0.04 ‰ on one or the other side of the curve would be found. Actually, though, the scatter is not much greater than that which should have been expected from the errors in titration and bridge measurements, and further there are no systematic differences between the points determined at 30° C. and those determined at 40° C. Therefore, a calibration curve determined at one temperature may be used at another temperature, or at any rate the regulating temperature of the bath need not be adjusted accurately to a specified value.

A calibration curve can be fairly well represented by a second-degree equation of the type

$$S = S_1 [1 + \alpha (s - s_1) + \beta (s - s_1)^2]$$

in which S is the salinity of any sample corresponding to a slide-wire reading of s, S_1 is the salinity of a known sample corresponding to an arbitrarily selected slide-wire reading s_1, and α and β are numerical coefficients.

For the calibration curve obtained from the 220 titrated samples, the equation is

$$S = 35 [1 + 295.7 \times 10^{-6} (s - 699.5) + 46 \times 10^{-9} (s - 699.5)^2] \quad (10)$$

This can be compared with the theoretical equation (7) by equating s' to 699.5 from which it follows that $n = 1/7{,}699.5$ and $m = 1/7{,}399.5$, and equation (7) becomes

$$S = 35 [1 + 299.6 \times 10^{-6} (s - 699.5) + 41.1 \times 10^{-9} (s - 699.5)^2] \quad (11)$$

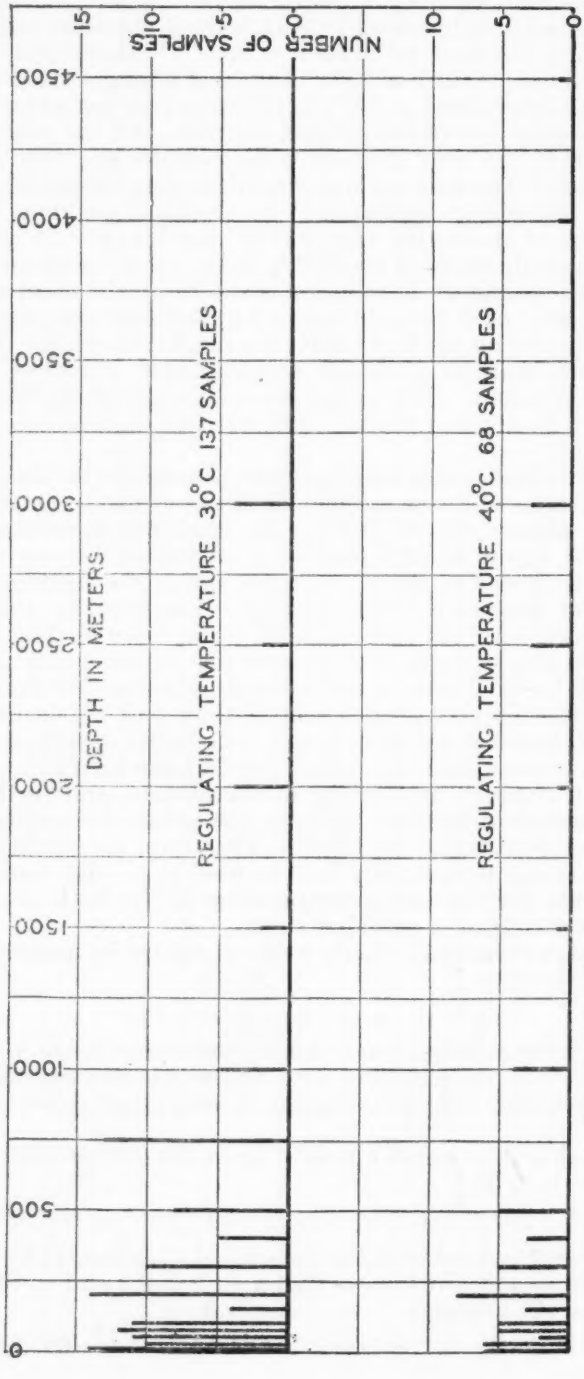


FIGURE 10.—*Vertical distribution of calibration samples used in Carnegie equipment*

The agreement between equations (10) and (11) is good considering again the previously discussed uncertainty of 4×10^{-6} in the first-degree coefficient of the theoretical equation.

In the development of the theoretical equation it has been assumed that the resistance in the X arm of the bridge is made up entirely of the resistance of the solution in the X cell. Actually, of course, there is some small fixed resistance embodied in the cell terminals and leads. A generous estimate of this fixed resistance would be 0.1 per cent of the resistance of the X arm, or about 0.2 ohm. If such were the case the first-degree coefficient would only be changed by about 0.3×10^{-6} and the second-degree coefficient would only be changed by about 0.1×10^{-9}. In view of the other uncertainties, it is justifiable to neglect this fixed resistance.

The experimental results obtained on the *Carnegie* differ most from the second-degree equation in the vicinity of slide wire reading equal to 800. Here a number of points fall above the curve of the equation. This may have been caused by a lack of uniformity in that part of the slide wire, although this is not indicated by the manufacturer's report. About a dozen of the outstanding departures from this part of the curve were investigated as to geographical origin. Two were found to have been evaporated or prepared samples, and the other ten which were true sea-water samples came from the upper 200 m of stations No. 46, 47, 91, and 161. Curiously enough, these stations all have about the same latitude (between 9° south and 16° south), while their longitudes vary from that of Easter Island to that of the Samoan Islands. Although the coincidence is suggestive, no conclusions regarding salt ratios can be drawn since these data are far too meager.

Other systematic deviations from the second-degree equation occur, but have no apparent relation to geographical position. One can assume that such deviations are caused either by lack of uniformity in the slide wire or by variation in composition of the salt. However, if the latter assumption is made, it requires that the composition be an irregular function of the salinity. Such a relationship seems highly improbable. In view of these considerations and the above discussion of the theoretical form of an equation for the calibration curve, the bridge measurements made on the *Carnegie* were converted into salinities by the use of the second-degree equation given, and a table of corrections based on systematic variations of the titration comparisons from that curve. When such corrections are applied to the second-degree equation, 212 out of the 219 titration comparisons fall within a difference of 0.04 ‰. This seems to show an even greater constancy of salt composition than has been assumed in the past and leads one to question the accuracy of chemical analyses of sea water as published in the past. Such published analyses indicate that if solutions of each were adjusted to equal concentration the salinities as given by titration would differ in some cases in the first decimal place of parts per thousand. Obviously no such variations were encountered in the cruise of the *Carnegie*.

The authors are not aware of the existence of data on the variation of conductivity of sea water of constant concentration with variation in composition. Since the ratio of mobility to weight of

the constituent ions differs, it is true that the conductivity will n be independent of the composition. However, there are many kin of ions present, and as dissociation is never complete, the complexi of the problem precludes an accurate quantitative theoretical analys and one can only say that the variation in conductivity is small an probably the conductivity method comes closest, of available fie methods, to the measurement of total salt.

3. DISCUSSION OF TEMPERATURE COEFFICIENT

The previously mentioned design feature of having similar electro lytic cells form two adjacent arms of the bridge has, as one of it objectives, lessening the importance of accurate temperature contro In other words, it was hoped that by this device the effective tempera ture coefficient of the instrument would be very much less than tha of sea water. The efficacy of this arrangement was tested on th *Carnegie* as follows: When the regulating temperature of the wate bath was changed from 30° to 40° C., Copenhagen standard water which was used as the final standard at the end of the last 30° C routine salinity run, was left in the cells and was remeasured on th following day at 40° C., with the auxiliary resistance Q having th same setting as was used at 30° C. The differences in slide-wir readings were converted into differences in salinity and considered to be the effect produced by a 10° C. change in temperature of t sample. This was done on a basis of 1.0 unit on the slide wire corre sponding to a change of 0.01 ‰ in salinity. This procedure furthe was based on the assumptions that during the period of about 24 hours the salinity of the solution in the auxiliary or Y cell did not change and that the cell constants did not change. Such assumptions were justifiable as only a rough determination was made. The slide-wire reading at the balance of the initial standard was 698.5 in each case, by definition. Either because of changes in cell constants or changes on the auxiliary cell solutions, the slide-wire readings were slightly different for the final standard than for the initial standard. If it is assumed that these changes were permanent, the slide-wire readings for the final standard should be used, whereas if these changes are assumed to have been temporary and to have disappeared (such as might be the case if part of the auxiliary cell solution vaporized during the run and condensed again afterward), then the slide-wire readings of the final standard should be used. Following the remeasurement of the final standards at 40° C., they were withdrawn and replaced by other samples, originally having the same salinity, and another series of slide-wire readings taken. Assuming that no change in salinity of the final standards had occured, the final standard as remeasured should be used. If it be assumed that the final standard had changed in salinity, then the fresh standard should be used. Thus there are four combinations per cell which will give a temperature coefficient of salinity. Their means have been taken as shown in Table 1.

TABLE 1.—*Data for temperature coefficients of salinity for cells A, B, and C*

Cell	Observation	Temperature	Standard	Q	Slide-wire reading	Temperature coefficient	
						From—	Value
		°C.			d		‰ per °C.
	I	30	Initial	1.913	698.5	I and III	0.0078
	II	30	Final	1.913	698.1	I and IV	47
	III	40	do	1.913	706.3	II and III	82
	IV	40	New	1.913	703.2	II and IV	51
n for cell							.0064
	I	30	Initial	3.048	698.5	I and III	.0041
	II	30	Final	3.048	698.2	I and IV	67
	III	40	do	3.048	702.6	II and III	44
	IV	40	New	3.048	705.2	II and IV	70
n for cell							.0056
	I	30	Initial	3.208	698.5	I and III	.0138
	II	30	Final	3.208	698.7	I and IV	116
	III	40	do	3.208	712.3	II and III	136
	IV	40	New	3.208	710.1	II and IV	114
n for cell							.0126

These temperature coefficients, even if accurately determined, ould only apply with the same settings of the auxiliary resistance As the settings given above approximately represent ohms and the resistance of the cells were about 250 to 300 ohms each, it is n that the uncompensated sea-water resistance was about 1 per nt of the resistance of the unknown. Taking the temperature efficient of electrical conductivity of sea water as 3 per cent per gree centigrade, the temperature coefficient of salinity of the bridge ould have been expected to be of the order of 0.0003×35.00 or about 01 ‰ per degree centigrade. The general agreement between the perimental and calculated values indicates that the temperature efficient of the bridge arm containing the Y cell differed from that the arm containing the X cell by not more than 3 parts in 10,000. his would not be true generally, but would depend upon the differ- ce in cell constants of the X and Y cells and upon the ratio of the sistance of Q to the resistance of the sea water in the Y cell. It ay be noted, however, that had a wire resistance been used in place sea water in the Y cell, the temperature coefficient would have en in the neighborhood of 0.03×35 or about 1 ‰ per degree ntigrade. It should be understood that the wire resistances in e bridge were of manganin, having a negligible temperature co- ficient, and that when measurements were made the X and Y cells ere accurately at the same temperature.

VI. RECOMMENDED CHANGES IN CONSTRUCTION

Practical experience with the salinity bridges under actual field nditions suggests that the instrument might be improved somewhat y making a few minor changes. The following recommendations garding future construction are therefore made.

In a multiple X cell bridge (that is, one having more than one cell for unknown solutions) it is necessary to change the setting of the auxiliary resistance Q from one value to another as the different cells are used. It therefore is necessary, when returning to a given X cell, to be able to duplicate not only the original setting of Q corresponding to that particular cell, but also to have the resistance indicated by that setting the same as the resistance for the original setting. The uncertainty of any measurement will hence be affected if the resistance of the auxiliary switch contacts is uncertain. While it would take an uncertainty in contact resistance of nearly 0.1 ohm to produce an uncertainty in the measurement of about 0.01 ‰ salinity, and while it is easily possible to keep the uncertainty in switch contacts below this figure, it is also true that a defective switch or one of poor construction can develop such an uncertainty. Good workmanship is important in the construction of these switches. A recommended design is one in which the total resistance is soldered into the circuit and individual coils are successively short circuited by a multiple spring-leaf dial switch having double diametrical segment contacts. Such an arrangement places two contacts in parallel and, as it is improbable that both contacts will become defective simultaneously, the chance of troublesome switch contacts is thereby reduced. Even with good design and workmanship, the switches of the auxiliary resistance should occasionally be inspected and tested for uncertainty of resistance. The constancy of the switch contact resistance is improved if the contacts are kept lubricated with clean oil.

The size of the electrolytic cells might well be reduced to half the dimensions used in the first three instruments. This would reduce the volume to about one-quarter and would not only mean a saving in standard water, but would leave more of the unknown sample for other determinations. A small saving would result from the reduced size of the electrodes. The resistance of the cell would be about doubled, thus reducing the importance of contact resistances. Less space would be needed per cell in the water bath, and possibly less time would be required for the sample to come to the regulating temperature. If the voltage of the test current supply is kept the same, the heat produced by the test current per cell will be halved and, as the rate of dissipation of this heat would probably not be as much affected, the test current would probably have a smaller effect on the temperature of the sample. It is realized that greater care would be necessary in the manufacture of the smaller cells, but it is believed that the advantages to be gained make the change desirable.

As it was estimated that 15 minutes were required for a sample to reach the temperature of the water bath under conditions of low room temperature, and as about two minutes are required for measurement, rinsing, and refilling, it seems best to have six X cells. The number of samples to be measured per run will determine to some extent the optimum number of cells.

It is probable that the test current dissipated about 0.005 watt per cell and for future construction it is recommended that the test current be reduced to one-half, or less, of that previously used. The resulting loss in sensitivity would be more than counterbalanced by the use of telephone receivers tuned to the frequency of the test current; that is, 1,000 cycles. They should still, of course, be selected

to have about the same impedance as the bridge arms. The tuning should be done at the factory or in the laboratory and should not be adjustable, as unnecessary adjustments are undesirable in any field instrument.

Even with careful construction certain inspections should be made from time to time and minor repairs may be necessary in the field. All circuits should therefore be made accessible, even though ordinarily protected. Hence, ample doors or removable covers should be placed in the case of the instrument back of the panels.

The range of salinities covered by the bridge will be governed largely by the purpose to which it is to be put, and by the nature of the expedition which will use it. If measurements are to be made in in-shore waters, or in the vicinities of the mouths of large rivers, a lower limit of 28 ‰ salinity or less should be selected. However, if measurements are to be made chiefly in the open seas, the lower limit should be at least 30 ‰. This would give an upper limit of about 40 ‰. A point to be remembered in selecting the salinity range is that that portion of the range which is below the salinities actually encountered at sea is wasted, whereas that portion which is above the salinities found in the sea can be used in evaporation work. It might be advisable to calibrate an instrument for two overlapping ranges. If such a procedure is followed it should be remembered that the deep water in most ocean areas is between 34.50 and 35.00 ‰ in salinity. It would be well, therefore, to include this in the overlap. Recommended ranges are 25.25 ‰ to 35.25 ‰ and 33.50 ‰ to 43.50 ‰. In this recommendation the lower limit of the upper range and upper limit of the lower range are stressed, the other two limits being given merely to indicate the approximate total range of the calibrations. The transfer from one range to another may be accomplished by changing only the concentration of the solution in the auxiliary cell. However, if such a change is to be made frequently, much time will be saved by having two Y cells, either of which may be switched into the circuit, rather than actually changing the solution in a single Y cell.

A warning should be given that a calibration curve can not be shifted parallel to itself without introducing errors. These errors arise from the fact that a change of one division of the slide-wire reading at balance means a change of resistance of about 2/7,500 at the middle of the slide wire, whereas at the end of the slide wire the same change in setting means a change in resistance of 1/7,000 plus 1/8,000. Differently expressed, the middle 250 divisions of the slide wire correspond to a change in salinity which is about 0.3 ‰ more than the change in salinity correspodning to the lower 250 divisions of the slide wire. It will be seen, then, that in the case of two overlapping ranges, calibration points on the overlap determined on one of the ranges can not be transferred to the other range by a constant displacement, but must be determined by actual measurement on both ranges.

VII. SUMMARY

The electrical salinity bridge described was the result of the oceanographic demands of the International Ice Patrol in the North Atlantic Ocean.

An accurate and rugged instrument suited to severe sea conditions was developed, and instruments built and used with satisfactory results.

The instrument as described compares well in performance with titration measurements, is capable of individual measurements accurate to within 0.02 ‰, and is well adapted to the measurement of total salt.

The temperature compensation has been tested and found to be effective and in agreement with the results expected from theory.

The calibrations of actual instruments have been compared and can be fairly well predicted for similar instruments built in the future.

Experience with the first three instruments built has led to the recommendation of several changes in details of construction considered to be improvements over the first models.

WASHINGTON, June 17, 1930.

NOTE ON THE INDIVIDUALITIES OF ANHYDROFRUCTOSE AND DIFRUCTOSE ANHYDRIDE

By R. F. Jackson and S. M. Goergen

ABSTRACT

Almost simultaneously with the publication of Research Paper No. 79 of the Bureau of Standards in which is described a crystalline difructose anhydride, Irvine and Stevenson published a description of a new anhydrofructose. These two substances showed such similar physical properties as to suggest their identity. It is now shown that difructose anhydride has a different molecular weight and melting point from anhydrofructose. The two substances are, therefore, not identical.

In the course of an investigation [1] of the hydrolysis of inulin by sulphuric acid in aqueous solution, the authors isolated a group of nonreducing disaccharides, one of which was obtained in crystalline form and shown to be a difructose anhydride.

Almost simultaneously with the release of this article Irvine and Stevenson [2] published a description of a crystalline anhydrofructose which they isolated in 20 per cent yield from inulin. The striking similarity in physical properties between these two sugars raises the question whether they are not identical. The respective properties previously published are shown in the following table:

	Anhydrofructose	Difructose anhydride
$[\alpha]_D^{20}$ (acetate)	+1.5	+0.5.
$[\alpha]_D^{20}$ (sugar)	+30.17	+27.0.
Melting point (acetate)	123°	{125° (sinters). 137° (melts).
Melting point (sugar)	143–145°	
Molecular weight	162	
Crystallizes	Transparent spheroids	Laminated spheres.

An important difference is the behavior of the respective sugars when exposed to air. Anhydrofructose is deliquescent, while difructose anhydride remains dry even in an atmosphere of high humidity. The latter will even crystallize from aqueous solutions when evaporating in open vessels at room temperature.

In our study of difructose anhydride we had isolated it in the form of its hexa-acetate. The determination of the molecular weight of the acetate by measurement of the depression of freezing point of

[1] B. S. Jour. Research, 3, p. 27; 1929. (RP 79.)
[2] J. Am. Chem. Soc., 51, p. 2197; 1929.

benzene showed so definitely that it was the acetate of a disaccharide that we deemed it unnecessary to determine the molecular weight of the free sugar. In order, however, to differentiate conclusively between this sugar and the anhydrofructose of Irvine and Stevenson, we have determined the molecular weight and melting point of difructose anhydride. *Mol. wt.*, Subs., 1.0103; water, 20.298; ΔT, 0.307°. Mol. wt., calcd., 324; found, 307. Mpt., 162–164°. There is therefore no question of the individualities of these respective sugars.

WASHINGTON, June 14, 1930.

THE CHLOROPLATINATE-CHLOROPLATINITE ELECTRODE

By Edgar Reynolds Smith

ABSTRACT

A platinum electrode immersed in tenth normal potassium chloride solution containing a mixture of potassium chloroplatinate and potassium chloroplatinite has a definite electromotive force corresponding to the electrode reaction $PtCl_4^{--} + 2\ Cl^- = PtCl_6^{--} + 2e^-$. This electromotive force was measured against the tenth normal calomel electrode and extrapolated to pure tenth normal potassium chloride solution. The experimental results show that this electrode functions reversibly.

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I. INTRODUCTION

An investigation by Miller and Terrey [1] has shown that an inert electrode immersed in a solution containing sodium chloroplatinate and sodium chloroplatinite acquires a definite potential. Their reference electrode was a calomel electrode containing sodium chloride instead of the usual potassium chloride and their cell may be formulated as follows

$$-\ Hg\ |\ HgCl,\ NaCl\ |\ NaCl + Na_2PtCl_6 + Na_2PtCl_4\ |\ Pt +$$

The cell reaction is

$$2\ Hg + Na_2PtCl_6 = 2\ HgCl + Na_2PtCl_4$$

The electrochemical reaction at the platinum electrode is

$$PtCl_6^{--} + 2e^- = PtCl_4^{--} + 2\ Cl^-$$

Since this electrode represents a new type of chloride ion electrode as compared with the usual forms, such as Cl_2 (g), Cl^-, Ag | AgCl, Cl^- and Hg | HgCl, Cl^-, and presents the unusual feature that no change in charge occurs during the oxidation and reduction of the complex platinum ions, some further experimental tests of this electrode may be of interest.

In this work the potassium salts of chloroplatinic and chloroplatinous acid were used and the reference electrode was the calomel half cell with tenth normal potassium chloride solution. Liquid junction potentials were made negligible by using tenth normal potassium chloride as the solvent for the platinum salts and by using only

[1] Miller and Terrey, J. Chem. Soc. (London), p. 605; 1927.

relatively small concentrations of the latter, thus maintaining a practically constant thermodynamic environment.[2] The cell can be written

$$-\mathrm{Hg}|\,\mathrm{HgCl},\ \mathrm{KCl}\ (0.1)\left|\begin{matrix}\mathrm{KCl}\ (0.1)\\ \mathrm{PtCl_4^{--}}\\ \mathrm{PtCl_6^{--}}\end{matrix}\right|\begin{matrix}\\ \left\{\begin{matrix}\text{small concns.}\\ \text{compared with}\\ \text{0.1 normal.}\end{matrix}\right\}\end{matrix}\Bigg|\,\mathrm{Pt}+$$

The expression for its electromotive force is

$$E=E_0-\frac{RT}{2F}\log_e\frac{(\mathrm{PtCl_4^{--}})}{(\mathrm{PtCl_6^{--}})} \tag{1}$$

where the terms in parentheses are the activities of the chloroplatinite and chloroplatinate ions. Since activity coefficients depend on the ionic strength [3] of the solution, the data obtained were correlated by means of the empirical equation

$$E=E_0-\frac{RT}{2F}\log_e\frac{(PtCl_4^{--})}{(PtCl_6^{--})}+k\sqrt{\sigma} \tag{2}$$

where the terms in parentheses now represent actual concentration and σ is the ionic strength of the solution. If we let

$$E'=E+\frac{RT}{2F}\log_e\frac{(PtCl_4^{--})}{(PtCl_6^{--})} \tag{3}$$

Equation (2) becomes

$$E'=E_0+k\sqrt{\sigma} \tag{4}$$

This equation was tested for the system at 35° C.

II. APPARATUS

The cell is shown in Figure 1. The inert electrode consisted of a piece of lightly platinized platinum gauze 1 by 2.5 cm. The cell was immersed in a thermostat containing well-stirred liquid petrolatum and provided with a mercury contact regulator and a heater. The temperature was held constant at 35° ± 0.05° as measured with a calibrated thermometer graduated in 0.2° divisions and read with an attached magnifying glass.

The electromotive force measurements were made with a Leeds & Northrup type K potentiometer and a certified standard cell.

III. MATERIALS

The potassium chloride was prepared by once recrystallizing the "c. p." salt from water. The salt thus obtained was dried and heated to incipient fusion in a platinum dish.

[2] Washburn, Principles of Physical Chemistry, McGraw-Hill Book Co., New York; 1915.
[3] Lewis and Randall, Thermodynamics and the Free Energy of Chemical Substances, McGraw-Hill Book Co., New York, 1923.

Calomel was prepared by dissolving purified mercury in cool nitric acid and precipitating with hydrochloric acid. The mercury used was "virgin" mercury which had been thoroughly washed with dilute nitric acid and subsequently twice distilled, first in a Hulett still and then in a vacuum still. The precipitated mercurous chloride was washed free from acid by decantation, filtered by suction, washed repeatedly with tenth normal potassium chloride, and made into a paste with the latter and the purified mercury.

For the preparation of the platinum salts, platinum sponge and a 10 per cent solution of pure chloroplatinic acid were kindly supplied by Dr. E. Wichers of this bureau. The platinum sponge had been purified for use in the preparation of thermoelements and was free of

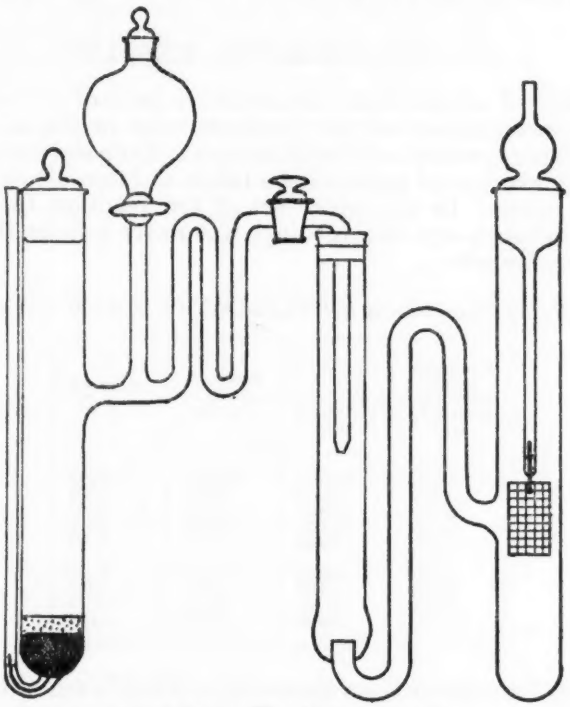

FIGURE 1.—*The electrode system*

heavy metal impurities as far as could be detected by spectrographic determination. It probably contained small amounts (not over 0.01 per cent) of alkali salts.

For the preparation of the potassium chloroplatinite, platinum sponge was dissolved in aqua regia, the solution evaporated several times with hydrochloric acid to expel nitric acid, and subsequently reduced to chloroplatinous acid by means of sulphur dioxide according to the method of Heraeus [4] as described by Wöhler and Frey.[5] The salt obtained by adding potassium chloride was recrystallized first from distilled water, then from hydrochloric acid, and finally

[4] Heraeus, Ber., **37**, p. 1360; 1904.
[5] Wöhler and Frey, Z. Elektrochem., **15**, p. 133; 1909.

dried at 80° to 90° to constant weight. The platinum content of this salt was determined by precipitating with hydrogen sulphide in acid solution and igniting the precipitated sulphide to metal. The value found was 47.13 per cent as compared with the theoretical value of 47.01 per cent.

The potassium chloroplatinate was prepared from the 10 per cent solution of chloroplatinic acid. This solution was part of a stock solution prepared from platinum sponge, of the same quality as that previously mentioned, by anodic oxidation in concentrated hydrochloric acid. The chloroplatinate was obtained by adding a saturated acidified solution of potassium chloride.

The solutions were prepared by weighing the dry salts and the water, the concentrations being expressed in formula weights per 1,000 g of water.

IV. EXPERIMENTAL RESULTS

The measured values of the electromotive force of the cell, together with the concentrations of the platinum salts in the solutions, are shown in Table 1, which is self-explanatory. Each electromotive force value is the average of ten readings taken at intervals over a period of several hours. In any given set of ten readings the maximum difference between any two readings was never greater than 0.2 mv and was usually less.

TABLE 1.—*Emf of cell containing K_2PtCl_4 and K_2PtCl_6 in 0.1 M KCl solution at 35°*

Concentration of K_2PtCl_4 mole per 1,000 g H_2O	Concentration of K_2PtCl_6 mole per 1,000 g H_2O	Total concentration of Pt salts	Measured emf (volt)
0.000483	0.000520	0.001003	0.45852
.000252	.000752	.001004	.47200
.001956	.000555	.002511	.44095
.001248	.001251	.002499	.45806
.000500	.002009	.002509	.47620
.002488	.002511	.004999	.45849
.003957	.001017	.004974	.44044
.008999	.001026	.010025	.43034
.007504	.002483	.009987	.44456

In Table 2 are given the values of $E+(RT/2F)\log_e (PtCl_4)/(PtCl_6)$ at round concentrations, together with the corresponding values of the square root of the ionic strength of each solution.

TABLE 2.—*Emf and ionic strength data calculated for round concentrations*

Total concentration of Pt salts (Pt) in 0.1 *N KCl* solution mole per 1,000 g H_2O	$\sqrt{\sigma}$ / $\sqrt{0.1+3(Pt)}$	E' / $E+\frac{RT}{2F}\log_e\frac{(PtCl_4^{--})}{(PtCl_6)^{--}}$
0.001	0.321	0.4575
.0025	.328	.4578
.005	.339	.4584
.01	.361	.4592

V. DISCUSSION

For very dilute solutions of electrolytes the activity coefficient, γ, of an ion of valence z is given by the equation

$$\log_{10} \gamma = 0.52\ z^2\ \sqrt{\sigma} \qquad (5)$$

where σ is the ionic strength. If this equation were valid for the range of concentrations used in this investigation the activity coefficients of the chloroplatinate and the chloroplatinite would be equal and cancel each other and the value of E_0 calculated from equation (1) should be the same for each measurement. However, the total concentration of every solution used was greater than tenth normal and the values of E_0 from equation (1), or of E' from equation (3), show a tendency to increase with increasing ionic strength, as is seen in Table 2. For this reason, the values of E' were plotted, as shown in Figure 2, against the square root of the ionic strength, in order to extrapolate for the value of E_0 in tenth normal potassium chloride

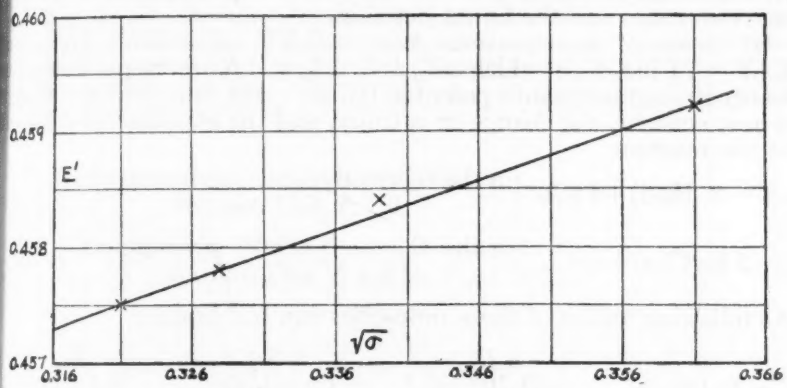

FIGURE 2.—*Plot of E' against* $\sqrt{\sigma}$

solution. The value thus obtained, $E_0 = 0.4573$ v., is the electromotive force of the cell

$$\mathrm{Hg} \mid \mathrm{HgCl},\ \mathrm{KCl}(0.1) \left| \begin{matrix} \mathrm{PtCl_4^{--}}(A) \\ \mathrm{PtCl_6^{--}}(A) \end{matrix} \right| \mathrm{Pt\ at\ 35°}$$

in which (A) is the activity of the complex platinum ions in the thermodynamic environment of pure 0.1 normal potassium chloride solution. This should not be confused with the "standard" or "molal" electrode potential, since the latter is ordinarily restricted to an environment of pure water.

Since this work and that of Miller and Terrey are the only investigations that have been carried out on this electrode system, a comparison of results is of interest. The comparison, however, is possible for only one of their measurements where they used the cell

$$\mathrm{Hg} \mid \mathrm{HgCl},\ \mathrm{NaCl}(1\ N) \left| \begin{matrix} \mathrm{NaCl}\ (0.1\ N) \\ \mathrm{PtCl_4^{--}}(0.0009987) \\ \mathrm{PtCl_6^{--}}(0.001462) \end{matrix} \right| \mathrm{Pt\ at\ 25°}$$

In this cell the total concentration of platinum salts is 0.00246 molal and the thermodynamic environment is tenth normal sodium chloride solution. The conditions are, therefore, comparable with those

under which the data given in the second row of Table 2 were obtained E (measured) for this cell is 0.5058 v. The liquid junction potential is 0.0105 v. and $(RT/2F)\ \log_e\ (PtCl_4^-)/(PtCl_6^-) = -0.0049$. We therefore, have $E' = 0.5058 + 0.0105 - 0.0049 = 0.5114$ v. Taking the electrode potential of the normal calomel electrode with sodium chloride to be the same as with potassium chloride (0.2805 v.)[6] the corrected potential at the platinum electrode is 0.7919 v. Miller and Terrey found 21,720 cal. for the heat evolved during the reaction $2\ Hg + PtCl_6^- = 2\ HgCl + PtCl_4^-$ by measuring the temperature coefficient of electromotive force of the cell. Using this value in the Gibbs-Helmholtz equation we find $E' = 0.4582$ for our cell at 25° with a total platinum molality of 0.0025 in 0.1 normal potassium chloride. The value for the tenth normal calomel electrode[6] is 0.3334 v. and, therefore, the corrected potential at the platinum electrode is 0.7916 v., which compares very favorably with the value 0.7919, obtained above from the work of Miller and Terrey. This favorable agreement depends largely on the choice of values for the potentials of the reference electrodes and the liquid junction.

By means of the equations $\Delta Z_0 = -E_0NF$, $\Delta Z_0 = \Delta H_0 - T\Delta S_0$, and $E_0NF = RT\ \log_e K$, in which ΔZ_0, ΔH_0, ΔS_0, and K are, respectively, the change in thermodynamic potential (Gibbs's zeta function), the change in heat content, the change in entropy, and the equilibrium constant for the reaction

$$2\ Hg(l) + PtCl_6^- \left\{\begin{array}{c}\text{in the thermodynamic environment of} \\ 0.1\ N\ KCl\ \text{solution}\end{array}\right\}$$

$$= 2\ HgCl(s) + PtCl_4^- \left\{\begin{array}{c}\text{in the thermodynamic environment} \\ \text{of 0.1 } N\ KCl\ \text{solution}\end{array}\right\} \text{at } 35°$$

the following values of these properties can be obtained

ΔZ_0	ΔH_0	ΔS_0	K
−21,100 cal.	−21,700 cal.,[7]	−1.9 cal./deg.	9.1×10^{14}

IV. SUMMARY

The electromotive force of the cell

$$-Hg \left| HgCl,\ KCl(0.1),\ \begin{array}{c}KCl(0.1) \\ K_2PtCl_4(m_1) \\ K_2PtCl_6(m_2)\end{array} \right| Pt+ \text{ at } 35°$$

where m_1 and m_2 are small compared with 0.1 has been measured for values of $(m_1 + m_2)$ ranging from 0.001 to 0.01. The equation

$$E = E_0 - (RT/2F)\ \log_e m_1/m_2 + k\sqrt{\sigma}$$

in which k is a constant and σ is the ionic strength of the solution, represents the experimental data and gives a value of 0.4573 v. for E_0 in tenth normal potassium chloride solution. From this value of E_0 and the known change in heat content accompanying the cell reaction, the corresponding change in thermodynamic potential, change in entropy and the equilibrium constant were calculated.

WASHINGTON, February 20, 1930.

[6] Int. Crit. Tables, 6, p.332.
[7] Miller & Terrey; see footnote 1, p 735.

A NEW CRYSTALLINE CALCIUM CHLORIDE COMPOUND OF α-*d*-GULOSE AND ITS ROTATION AND MUTAROTATION IN AQUEOUS SOLUTION

By Horace S. Isbell

ABSTRACT

The optical rotation of α-*d*-gulose is determined from a new crystalline calcium chloride compound of α-*d*-gulose. The calcium chloride is removed from the compound very completely and quickly by means of dry silver oxalate, giving a pure gulose solution which exhibits mutarotation.

The equilibrium rotation of α-*d*-gulose $CaCl_2 \cdot H_2O$ varies widely with the concentration of the solution. It is shown that concentrated solutions upon dilution with water exhibit mutarotation which indicates that the equilibrium of the various forms of the sugar in solution is altered by a change in the concentration of calcium chloride. It is believed that this equilibrium disturbance is caused by the dissociation of the double compound of *d*-gulose and calcium chloride, which is further illustrated by the optical rotations of alcoholic solutions.

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I. INTRODUCTION

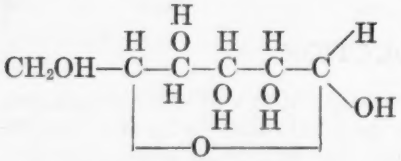
The determination of the optical rotation of any of the aldohexoses, which have not yet been obtained in the crystalline state, is of importance. Only three types of the aldohexose sugars (glucose, galactose, and mannose) have been obtained in crystalline form, and their rotations measured. In order to complete the data for calculating the optical rotations of the different asymmetric carbon atoms in the aldohexose sugars [1] the rotation of a fourth aldohexose was necessary. One of the less known hexose sugars, *d*-gulose, may be obtained as a pure sirup by the Kiliani [2] synthesis from xylose. A semicommercial

[1] H. S. Isbell, B. S. Jour. Research, 3, p. 1041; 1929.
[2] Kiliani, Ber., 18, p. 3066; 1885.

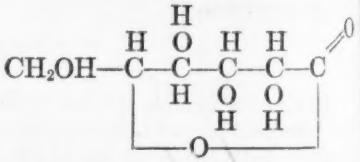
method for the preparation of xylose has been developed at the Nation Bureau of Standards [3] so that sugar is now available in large quantities which makes the *d*-gulose series a particularly attractive field for in vestigation.[4] *d*-gulose was first prepared by Fischer and Stahel by the reduction of gulonic lactone with sodium amalgam. The obtained a crude gulose sirup from which a crystalline phenylhydra zone was prepared. This compound was subsequently used for the purification of the sugar by Blanksma and van Ekenstein [6] who re moved the phenylhydrazine with benzaldehyde. Although the obtained a relatively pure product they were unable to bring the pur gulose sirup to crystallization. Subsequently by the same metho other investigators [7] including the author, have obtained simila results. Hence, it was evident that a radical departure from the previous method for the purification of the sugar was desirable. This led to the consideration of the coordination compounds of the sugars with inorganic salts. Recently J. K. Dale [8] prepared several new crystalline calcium chloride compounds of various sugars whose molecular rotations agree approximately with the rotations of the corresponding crystalline sugars. In the light of Dale's work the author decided to attempt the preparation of a calcium chloride com pound of *d*-gulose with the object of obtaining a crystalline derivative which would serve to establish some of the relations between structure and optical rotation in the hexose series.

II. α-*d*-GULOSE CALCIUM CHLORIDE

A crystalline calcium chloride compound was obtained upon evaporating in vacuo an aqueous solution of *d*-gulose containing about two molecular equivalents of calcium chloride. The new substance is dextrorotatory and mutarotates to the left indicating that it is an alpha [9] form of the sugar. This is the first crystalline compound which can be definitely assigned to the α-*d*-gulose series. As shown in Figure 1, it crystallizes in colorless prisms. It was shown to be a derivative of *d*-gulose by the separation of gulonic lactone in good yield after the oxidation of the sugar with bromine water. The oxidation was conducted according to the method devised by C. S. Hudson and the author,[10] and will be published in a subsequent paper.



α-*d*-gulose (1, 5)



d-gulonic (1, 5) lactone.

[3] Hall, Slater, and Acree, B. S. Jour. Research, **4**, p. 329; 1930.
[4] Originally a study of the *d*-gulose series was projected by C. S. Hudson, who has subsequently resigned from this bureau.
[5] Fischer and Stahel, Ber., **24**, p. 528; 1891.
[6] Blanksma and van Ekenstein, Chemisch Weekblad, **5**, p. 777; 1908.
[7] LaForge, J. Biol. Chem., **41**, p. 251; 1920.
[8] Dale, B. S. Jour. Research, **3**, p. 459; 1929; also J. Am. Chem. Soc., **51**, p. 2225; 1929.
[9] See Hudson, J. Am. Chem. Soc., **31**, p. 73; 1909.
[10] Hudson and Isbell, B. S. Jour. Research, **3**, p. 459; 1929; J. Am. Chem. Soc. **51**, p. 2788; 1929.

FIGURE 1.—*Photomicrograph of α-d-gulose $CaCl_2 \cdot H_2O$*

The calcium chloride compound has served for estimating the optical rotation of *α-d*-gulose; and has revealed some interesting properties relating to the influence of calcium chloride on the equilibirum of the different forms of the sugar in solution.

1. OPTICAL ROTATION OF *α-d*-GULOSE

The optical rotation of *α-d*-gulose was obtained from a freshly prepared solution of *α-d*-gulose $CaCl_2 \cdot H_2O$ after removing the calcium chloride with finely powdered silver oxalate. By that reagent the calcium chloride is removed very quickly and completely, and the resulting solution exhibits mutarotation. The mutarotation constant ($k_1+k_2=0.021$) for the solution agrees with the mutarotation constant for *α-d*-gulose $CaCl_2 \cdot H_2O$ ($k_1+k_2=0.019$). These values are also close to the value given by *d*-mannose ($k_1+k_2=0.019$),[11] the sugar which resembles *d*-gulose most closely. Since the rate of mutarotation of the pure gulose solution and the rate of mutarotation of the calcium chloride compound are nearly equal, it is possible to extrapolate the rotations observed after removing the calcium chloride to zero time and thus obtain the initial rotation of *α-d*-gulose. The initial specific rotation of *α-d*-gulose was found by this method to be $+61.6°$ (Table 1) which is equivalent to $[M]_D^{20}=+11{,}100$. The initial specific rotation of *α-d*-gulose $CaCl_2 \cdot H_2O$ was found to be $+37.7$ (Table 3) which is equivalent to $[M]_D^{20}=+11{,}650$. The difference in the molecular rotations just given appears to be only slightly more than the experimental error. Since the calcium chloride may increase the rotation of the sugar, the value obtained after removing the calcium chloride was chosen for the rotation of *α-d*-gulose and was used in a previous publication[12] for the calculation of the optical rotatory values for the various asymmetric carbon atoms in the aldohexose sugars.

[11] Hudson and Sawyer, J. Am. Chem. Soc. **39**, p. 475; 1917; also Dale, B. S. Jour. Research, **3**, p. 464; 1929.
[12] See footnote 1, p. 741.

TABLE 1.—*Mutarotation of α-d-gulose in water*

[1.2238 g of *α-d*-gulose $CaCl_2 \cdot H_2O$ were shaken with 2 g dry silver oxalate in 24.9550 g water; after filtration the rotations were read in a 2-dm tube. Density of the solution at 20° was 1.0095 g/ml. Calculated concentration = 0.7130 g gulose in 25.50 ml. $T = 20° \pm 0.5°$]

Time after the addition of water (in minutes)	Observed saccharimeter reading	$[\alpha]_D^{20}$ Calculated [1] for the gulose constituent	k_1+k_2 [2]
	°S		
0		[3] (+61.6)	
6	+6.43	+39.8	
8	+5.50	+34.0	0.020
10	+4.60	+28.5	.020
12	+3.80	+23.5	.020
14	+3.13	+19.4	.020
16	+2.35	+14.5	.021
18	+1.80	+11.1	.020
20	+1.22	+7.6	.021
25	−.02	−.1	.021
30	−.95	−5.9	.021
40	−2.25	−13.9	.021
50	−3.03	−18.8	.021
60	−3.50	−21.7	.021
∞	−4.27	−26.4	
Average			.0206

[1] $[\alpha]\frac{l}{D} = \frac{°S \times 0.3462}{lC}$, where l designates the temperature of the measurement, $°S$ is the observed saccharimeter reading, 0.3462 is the conversion factor, l the length of the solution in dm, C its concentration in g per ml at $t°$ which is equal to pd, where p is its concentration in weight per cent and d its density in g/ml at $t°$. (International Critical Tables, Vol. II, p. 334.)

[2] The numerical value for the mutarotation constant, $k_1+k_2 = \frac{1}{T}\log_{10}\frac{r_0 - r\infty}{r - r\infty}$ is calculated for all the observed values using the first observed value for r_0 and the final or constant value for $r\infty$.

[3] The initial rotation, which is placed in parentheses, is calculated by means of the mutarotation constant using the average numerical value, $k_1+k_2 = 0.0206$. If we let the unknown initial rotation be r_0, since the values of r (+39.8) at the time, t (6 min.) and the constant rotation, $r\infty$ (−26.4), are known, the equation, $k_1+k_2 = \frac{1}{t}\log_{10}\frac{r_0 - r\infty}{r - r\infty}$, is easily solved for r_0 (+61.6), the initial rotation. This value for r_0 is the extrapolated value for the rotation of the substance at zero time or at the moment at which it was put in solution. It is not the value used to calculate the numerical value of k_1+k_2.

TABLE 2.—*Mutarotation of α-d-gulose $CaCl_2.H_2O$ in water*

[Concentration = 1.2886 g of compound in 25 ml of solution; tube length, 2 dm; $T = 20° \pm 0.5°$

Time after making solution (in minutes)	Observed saccharimeter reading	$[\alpha]_D^{20}$ Calculated for the compound	k_1+k_2
	°S		
0		[1](37.9)	
2	+10.04	+33.7	
4	+8.84	+29.7	0.020
6	+7.84	+26.3	.020
10	+6.04	+20.3	.019
15	+4.19	+14.1	.019
20	+2.67	+9.0	.019
35	−.21	−.7	.019
45	−1.31	−4.4	.019
60	−2.31	−7.8	.019
∞	−3.32	−11.1	
Average			.0193

[1] Calculated as given under Table 1, above, using the following values: $k_1+k_2 = 0.0193$; $r = +33.7°$; $r\infty = -11.1°$; $t = 2$.

TABLE 3.—*Mutarotation of α-d-gulose $CaCl_2.H_2O$ in water*

[Concentration = 2.6592 g of α-d-gulose $CaCl_2.H_2O$ in 25 ml of solution; tube length, 2 dm; $T = 18.5 \pm 0.5°$ C.]

Time after making solution (in minutes)	Observed saccharimeter reading	$[\alpha]_D^{18.5}$ of compound	k_1+k_2
	°S		
0		[1](+37.7)	
5	+18.03	+29.3	
8	+15.28	+24.9	0.019
17	+9.18	+14.9	.018
22	+6.58	+10.7	.018
30	+3.48	+5.7	.018
44	+.13	+.2	.018
69	−2.72	−4.4	.017
∞	−4.47	−7.3	
Average			.0180

[1] Calculated as given under Table 1, p. 744, using the following values: $k_1+k_2=0.018$; $r=+29.3°$; $r\infty=-7.3°$; $t=5$.

TABLE 4.—*Mutarotation of α-d-gulose $CaCl_2.H_2O$ dissolved in aqueous 5 per cent calcium chloride solution*

[Concentration = 0.5536 g α-d-gulose $CaCl_2.H_2O$ in 25 ml of solution in which 1.25 g $CaCl_2.2H_2O$ had been previously dissolved; length of tube, 2 dm; $T = 20° \pm 0.5°$]

Time after making solution (in minutes)	Observed saccharimeter reading	$[\alpha]_D^{20}$ of compound	k_1+k_2[1]
	°S		
0		[2](38.5)	
3	+2.76	21.6	
4	+2.26	17.7	0.068
6	+1.46	11.4	.068
8	+.86	6.7	.069
10	+.38	3.0	.072
12	+.06	.5	.073
15	−.24	−1.9	.072
20	−.54	−4.2	.077
∞	−.71	−5.6	
Average			.070

[1] The value of k_1+k_2 in this experiment is larger than the value which was obtained for a water solution (Table 3). C. P. calcium chloride usually contains a trace of alkali which accounts for this larger value.

[2] Calculated as given under Table 1, p. 744, using the following values: $k_1+k_2=0.070$; $r=+21.6$; $t=3$ min.; $r\infty=-5.6$.

TABLE 5.—*Mutarotation of d-gulose after dilution with water and with aqueous $CaCl_2$*

[5 ml portions of a solution[1] containing 3.1740 g of d-gulose per 100 ml were diluted to 25 ml (1) with 5 per cent calcium chloride solution, and (2) with water. The rotations were then read]

Diluted with 5 per cent $CaCl_2$ solution[2]			Diluted with water		
Time after adding $CaCl_2$ solution (in minutes)	Observed saccharimeter reading (2 dm tube)	$[\alpha]_D^{20}$ of d-gulose	Time after adding water (in minutes)	Observed saccharimeter reading (4 dm tube)	$[\alpha]_D^{20}$ of d-gulose
	°S.			°S.	
5	−0.75	−20.5	3	−1.95	−26.6
7	−.60	−16.4	9	−2.00	−27.3
10	−.55	−15.0	20	−1.95	−26.6
23	−.50	−13.6	40	−1.95	−26.6
∞	−.45	−12.3	∞	−1.95	−26.6

[1] The solution of d-gulose was obtained by removing the $CaCl_2$ from α-d-gulose $CaCl_2.H_2O$ (1.3947 g in a final volume of 25.6 ml). This solution gave a rotation of −4.78 °S. in a 2 dm tube, $[\alpha]_D^{20} = -26.1$.

[2] The calcium chloride solution was prepared by dissolving 5 g of anhydrous $CaCl_2$ in sufficient water to give 100 ml. The mutarotation constants are not recorded because the salt contained a small amount of alkali which accelerated the mutarotation.

TABLE 6.—*Mutarotation of d-gulose $CaCl_2 \cdot H_2O$ after dilution with water at 18.5° C*

[10 ml of the solution shown in Table 3 containing 2.6592 g *d*-gulose $CaCl_2 \cdot H_2O$ in 25 ml were diluted to 100 ml with water and the mutarotation was followed in a 4 dm tube. Concentration = 1.0637 g in 100 ml of solution]

Time after adding water (in minutes)	Observed saccharimeter reading	$[\alpha]_D^{18.5}$ of compound	k_1+k_2
	° *S.*		
0		[1](7.3)	
3	−1.0	− 8.1	0.019
4.5	−1.05	− 8.5	.013
10	−1.15	− 9.4	.015
14	−1.25	−10.2	.017
25	−1.45	−11.8	.020
30	−1.55	−12.6	.018
35	−1.58	−12.9	0.17
50	−1.65	−13.4	
∞	−1.78	−14.5	
Average			.017

[1] Calculated as given under Table 1, p. 744, using the following values: $k_1+k_2=0.017$; $r=-8.1$; $r\infty=-14.55$; $t=3$.

TABLE 7.—*Mutarotation of d-gulose $CaCl_2 \cdot H_2O$ after dilution with ethyl alcohol at 18.5° C*

[10 ml of the solution shown in Table 2 containing 2.6592 g *d*-gulose $CaCl_2 \cdot H_2O$ in 25 ml were diluted to 50 ml with absolute ethyl alcohol, and the mutarotation was followed in a 2 dm tube. Concentration = 2.1274 g in 100 ml of solution]

Time after adding alcohol (in minutes)	Observed saccharimeter reading	$[\alpha]_D^{18.5}$ of compound	k_1+k_2
	° *S.*		
0		[1](−7.4)	
2	−0.85	−6.9	
4	− .75	−6.1	[2](0.012)
8	− .60	−4.9	.011
12	− .50	−4.1	.009
22	− .40	−3.3	.006
33	− .13	−1.1	.007
44	+ .10	+ .8	.008
75	+ .40	+3.3	.007
∞	+ .95	+7.7	
Average			.008

[1] Calculated as given under Table 1, p. 744, using the following values: $k_1+k_2=0.008$; $r=-6.9$; $t=2$; $r\infty=+7.7$. The calculated value agrees within the experimental error with the specific rotation of the solution (−7.3) prior to dilution.

[2] The temperature rose slightly upon adding the alcohol to the aqueous solution, which may account for the higher values of k_1+k_2 obtained for the first 10 minutes.

TABLE 8.—*Variation in rotation of α-d-gulose $CaCl_2 \cdot H_2O$ with concentration*

α-*d*-Gulose $CaCl_2 \cdot H_2O$	Concentration of $CaCl_2$	Initial $[\alpha]_D^{20}$	Equilibrium $[\alpha]_D^{20}$	Equilibrium [1] $[\alpha]_{MG}^{20}$	Rotation calculated by $[\alpha]_D^{20} = -15.4+0.78$ C.	Per cent [2] undissociated α-*d*-gulose $CaCl_2 \cdot H_2O$
g/100 ml	*g/100 ml*					
10.6368	3.82	+37.7	−7.3	−8.79	−7.1	15.3
5.1544	1.85	+37.9	−11.1		−11.4	8.1
4.4640	1.60	+37.6	−11.6	−13.99	−11.4	7.2
2.3592	.85	+38.0	−13.4	−16.21	−13.6	3.8
1.5640	.56	+37.3	−14.4		−14.2	1.9
.8856	.32	[3]+36.9	−14.9	−17.53	−14.7	.9
Average		+37.7				

[1] As a matter of record the rotations were measured for light of two wave lengths. $[\alpha]_D^{20}$ was determined from observations with a Bates saccharimeter using the conversion factor 0.3462; $[\alpha]_{MG}^{20}$ was determined from observations with a polariscope using the mercury green line ($\lambda=546$) as a source of light. The difference in rotations with light of different wave lengths is not abnormal.

[2] Approximate estimation as given on p. 751.

[3] Omitted from the average.

2. EQUILIBRIUM ROTATION OF d-GULOSE $CaCl_2 \cdot H_2O$

In the preceding paragraph under Table 8 it is seen that the "initial rotation" of α-*d*-gulose $CaCl_2 \cdot H_2O$ is not influenced markedly by variations in the concentration of the compound; while in the same table it is shown that the equilibrium rotation varies from −14.9 to −7.3 when the concentration of *d*-gulose $CaCl_2 \cdot H_2O$ is increased approximately from 1 to 10 per cent. The equilibrium rotation of the pure sugar in the absence of calcium chloride does not vary greatly, as shown in column 6 of Table 5; thus a solution containing 3.1740 g *d*-gulose in 100 ml gave $[\alpha]_D^{20} = -26.1$; 5 ml of this solution when diluted to 25 ml with water did not exhibit mutarotation and gave $[\alpha]_D^{20} = -26.6$.[13] Hence, we may conclude that the large variations in the equilibrium rotation of α-*d*-gulose $CaCl_2 \cdot H_2O$ are not produced by the variation in the concentration of the sugar, but rather by the calcium chloride.

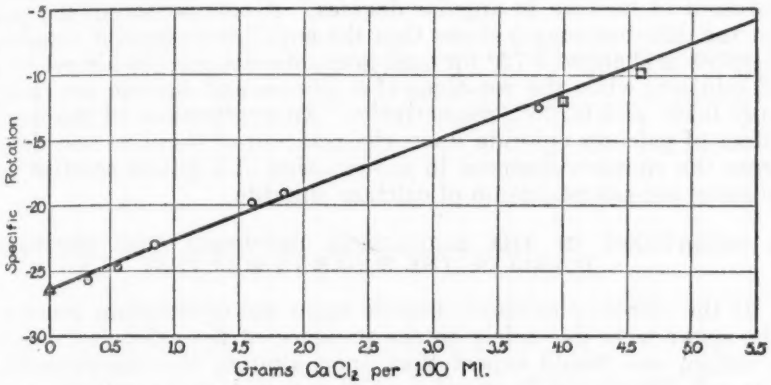


FIGURE 2.—*Effect of calcium chloride upon the equilibrium rotation of d-gulose*

The variation in the equilibrium rotation of *d*-gulose calcium chloride is nearly a linear function of its concentration which may be expressed by the following empirical equation:

$$[\alpha]_D^{20} = -15.4° + 0.78\ C \qquad (1)$$

where C is the concentration of *d*-gulose $CaCl_2 \cdot H_2O$ in g per 100 ml. This equation may be converted by equivalent weights to express the equilibrium rotation of *d*-gulose in the presence of calcium chloride. The following equation is thus obtained:

$$[\alpha]_D^{20} = -26.4 + 3.73\ m \qquad (2)$$

where $[\alpha]_D^{20}$ is the equilibrium specific rotation of *d*-gulose and m is the number of grams of anhydrous calcium chloride per 100 ml of solution.

The linear curve in Figure 2 represents the latter equation; the points marked with circles represent the rotations of *d*-gulose which

[13] The value $[\alpha]_D^{20} = -26.4$, which was obtained for the solution given in Table 1, agrees within the experimental error with the values given above. The value of $[\alpha]_D^{20} = -26.4$ for *d*-gulose is equivalent to $[\alpha]_D^{20} = -15.4$ for *d*-gulose $CaCl_2 \cdot H_2O$.

were obtained from different concentrations of the double compound of *d*-gulose and calcium chloride; the squares represent the rotation of *d*-gulose to which calcium chloride had been added, and the point marked with a triangle represents the rotation of a pure solution of *d*-gulose as obtained after removing the calcium chloride with silver oxalate.

It is interesting to compare the effect of calcium chloride upon the equilibrium rotation of *d*-gulose with its effect upon the rotations of other sugars. Murschhauser [14] found the specific rotation of *d*-gulose to be $+52.8°$ in water and $+56.0°$ in 2 *N* calcium chloride solution. The difference in rotation (3.2) is equivalent to an increase of 0.29 for each gram of calcium chloride per 100 ml of solution. Jackson and Gillis [15] found the rotation in ° *S* of a saccharimetric normal sucrose solution containing *m* grams of calcium chloride per 100 ml of solution is given by the equation: $R=100-0.339\ m$. This expression is equivalent to $[\alpha]_D^{20}=66.6°-0.226\ m$, where $[\alpha]_D^{20}$ is the specific rotation of sucrose in angular degrees. A comparison of the values for the different sugars shows that the equilibrium specific rotation of *d*-gulose is changed 3.73° for each gram of calcium chloride per 100 ml of solution, while the rotations of *d* glucose and sucrose are changed only 0.29° and 0.226°, respectively. An explanation of the marked effect of calcium chloride upon the rotation of *d*-gulose was derived from the changes observed in the rotation of a gulose solution upon altering the concentration of calcium chloride.

3. VARIATIONS IN THE EQUILIBRIA BETWEEN THE DIFFERENT FORMS OF THE SUGAR IN SOLUTION

If the effect of calcium chloride upon the equilibrium rotation of the sugar were due solely to the presence of the calcium chloride in solution, one would expect that upon altering the concentration of the salt the change in specific rotation would be practically instantaneous. However, if the calcium chloride altered the equilibrium between the different forms of the sugar in solution, the change in rotation would be slow and would occur at the same rate as the mutarotation of the sugar. A change in concentration of the calcium chloride and the sugar is easily obtained by diluting a concentrated solution. Measurements of optical rotation, after diluting a solution of *d*-gulose calcium chloride, clearly show a slow mutarotation, which follows approximately the course of a monomolecular reaction.

Figure 3 shows the mutarotation of the solution of α-*d*-gulose $CaCl_2 \cdot H_2O$ which was given in Table 3. After equilibrium was reached, a portion of the solution was diluted to 10 volumes with water. The mutarotation of this diluted solution is given in Table 6 and is illustrated in Figure 3 by the portion of the curve marked "diluted with water." Another portion of the solution in equilibrium was diluted to 5 volumes with absolute ethyl alcohol; the mutarotation of this portion is given in Table 7 and is illustrated in Figure 3 by the portion of the curve marked "diluted with alcohol." The solution upon dilution with water slowly becomes more levorotatory, while the solution upon dilution with alcohol slowly becomes less

[14] Murschhauser, Biochem. Z., **136**, p. 66; 1923.
[15] Jackson and Gillis, B. S. Sci. Paper No. 375, p. 164; 1920.

levorotatory. The extrapolated initial specific rotations of the portions diluted with water, ($[\alpha]_D^{20} = -7.3$), and with alcohol, ($[\alpha]_D^{20} = -7.4$), agree with the observed rotation ($[\alpha]_D^{20} = -7.3$) prior to dilution; that is, the solutions had practically the same specific rotation immediately after dilution as they had before dilution. The rate at which the rotation changes after diluting the concentrated solution with water ($k_1 + k_2 = 0.017$ at 18.5° C.) agrees with the rate of mutarotation of α-*d*-gulose $CaCl_2 \cdot H_2O$ ($k_1 + k_2 = 0.018$ at 18.5° C.), which indicates that the reaction is similar to the mutarotation of the sugar. As would be expected, the rotation of the portion diluted with alcohol changes more slowly than the rotation of the portion diluted with water. But of particular importance is the fact that a different equilibrium rotation ($[\alpha]_D^{20} = +7.7$) is reached from that given by an aqueous solution of similar concentration[16] ($[\alpha]_D^{20} = -13.7$), which indicates that the equilibrium existing in an alcoholic solution of *d*-gulose calcium chloride is different from the equilibrium existing in a water solution.

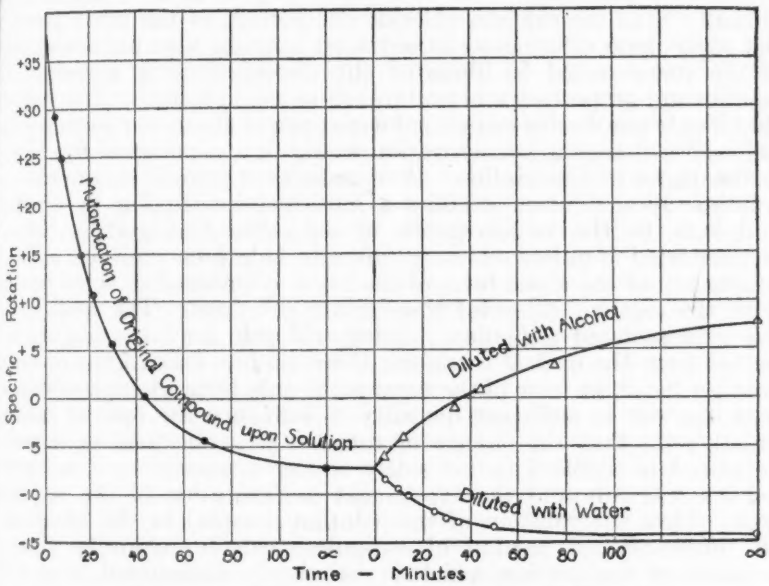


FIGURE 3.—*The mutarotation of d-gulose* $CaCl_2 \cdot H_2O$

4. DISSOCIATION OF α-*d*-GULOSE $CaCl_2$

The mutarotation which follows a change in the concentration of *d*-gulose calcium chloride indicates that in some manner the sugar equilibrium is disturbed by the change in concentration. Probably a sugar solution contains a number of isomeric ring forms in equilibrium.[17] The addition of a salt to the system further complicates the condition by forming molecular compounds with the various isomeric forms of the sugar. At this time it is not possible to state to what extent the various isomeric compounds actually exist, but

[16] Calculated from equation (1), p. 747.
[17] Cramer, "Les Sucres and Leurs Derives," p. 172, Gaston Doin & Co., Paris; 1927.

some of the molecular compounds may be obtained in the crystalli state.[18] It is probable that in dilute solution the compounds a largely dissociated into the sugar and calcium chloride. The degr of dissociation is influenced by the concentration and the solvent; change in the concentration or solvent alters the relative amounts dissociated and undissociated compounds. The dissociation ju mentioned should not be confused with the electrolytic dissociati of calcium chloride. The sugar may be associated with calciu chloride molecules, calcium ions or chloride ions; in the discussio that follows, the exact nature of the compound is immaterial thoug it is spoken of as a calcium chloride compound. According to th concept there are at all dilutions of *d*-gulose $CaCl_2$ less than infinit two classes of substances: (1) Associated gulose calcium chlorid and (2) completely dissociated α-and β-*d*-gulose in equilibrium. Th rotation of the solution is equal to the rotation of the undissociate *d*-gulose calcium chloride plus the rotation of the completely diss ciated α-and β-*d*-gulose in equilibrium. If a calcium chloride com pound of a particular form of a sugar is present in a much large quantity than the calcium chloride compounds of the other forms the sugar upon diluting a concentrated solution that particular for of the sugar would be liberated (by dissociation) in excess of th equilibrium proportion and mutarotation would follow. It is eviden that if only one double compound were present the mutarotation whic followed a change in concentration would be a measure of the chang in the degree of dissociation. A concentrated gulose calcium chlorid solution upon dilution exhibits a mutarotation similar in directio and rate to the mutarotation of α-*d*-gulose $CaCl_2 \cdot H_2O$. Hence concentrated *d*-gulose calcium chloride solutions contain a large proportion of the alpha form of the sugar (combined in some manne with the calcium chloride) than dilute solutions. The quantity the undissociated α-*d*-gulose calcium chloride may be roughly esti mated from the optical rotations, if we assume as an approximatio that (1) the alpha form of the sugar is the only form which is associate with the salt in sufficient quantity to influence the optical rotatio greatly; (2) that the change of rotation with dilution as shown i column 4 of Table 8 is due solely to the dissociation of α-*d*-gulos calcium chloride and the subsequent mutarotation of the sugar se free. Thus the rotation of the solution is equal to the rotation o the undissociated portion of α-*d*-gulose calcium chloride plus th rotation of the portion which is completely dissociated, and exist as an alpha beta equilibrium mixture. It was previously shown i column 3, Table 8, that the specific rotation of α-*d*-gulose $CaCl_2 \cdot H_2O$ is +37.7, and that it is fairly independent of dilution or the concen tration of calcium chloride. It was shown in paragraph 2 that th specific rotation of α-and β-*d*-gulose in equilibrium is also nearly independent of concentration and when expressed on the weight o *d*-gulose (180) equals −26.4 which is equivalent to −15.4 expressed on the weight of the compound, α-*d*-gulose $CaCl_2 \cdot H_2O$ (309). As shown in column 4, Table 8, the equilibrium specific rotation of *d*-gulose $CaCl_2 \cdot H_2O$ approaches with dilution the value just given; hence

[18] J. K. Dale obtained two crystalline calcium chloride compounds of *d*-mannose which he believes s ring isomers. See footnote 8, p. 742.

e specific rotation at infinite dilution is taken as −15.4. If we let equal the dissociated fraction of α-*d*-gulose $CaCl_2.H_2O$ then, $(1-X)$ equals the undissociated fraction and the specific rotation the solution is given by the following equation:

$$[\alpha]_D = 37.7\ (1-X) - 15.4\ X \qquad (3)$$

he values given in column 7, Table 8, for the undissociated *d*-gulose $CaCl_2$ were obtained from the data given in column 4 of e same table by the above equation. According to this method of lculation the undissociated portion of α-*d*-gulose $CaCl_2 \cdot H_2O$ at uilibrium in water solution increased from 0.9 to 15.3 per cent hen the concentration of calcium chloride was increased from 0.32 3.82 g per 100 ml. (Table 8.)

5. CRYSTALLIZATION OF α-*d*-GULOSE $CaCl_2.H_2O$

The dependence of the degree of dissociation of α-*d*-gulose $aCl_2 \cdot H_2O$ upon the concentration of calcium chloride and the sol- nt points to the conditions favorable for the crystallization of that bstance. Increasing concentrations of both calcium chloride and hyl alcohol shift the equilibrium rotation of *d*-gulose toward the tation of α-*d*-gulose $CaCl_2 \cdot H_2O$ which leads to the supposition at an excess of calcium chloride in concentrated alcoholic solution most favorable for the separation of α-*d*-gulose $CaCl_2 \cdot H_2O$. n application of these conditions resulted in a very marked improve- ent in the original method for the preparation of that product.

A concentrated aqueous *d*-gulose sirup is diluted with a solution of t least two equivalents of anhydrous calcium chloride dissolved in 5 per cent ethyl alcohol. After a short time crystalline α-*d*-gulose $CaCl_2 \cdot H_2O$ separates. Frequently crystallization does not start t once, but usually it may be started by carefully warming the solu- ion on a steam bath, or, if necessary, by nucleation. A second crop f crystals may be obtained by saturating the cold alcoholic solution ith ether and allowing to stand for several days. Although con- entrated gulose solutions are precipitated with 95 per cent ethyl lcohol they are almost miscible with alcoholic solutions of calcium hloride. The use of the alcoholic calcium chloride solution gives a ood yield of crystalline product which is difficult to obtain with queous solutions. The improved method is so satisfactory that the alt may be crystallized from the crude *d*-gulose sirup obtained from he reduction of gulonic lactone without previous purification by neans of the phenylhydrazone. If it is desired to prepare a con- iderable quantity of α -*d*-gulose the elimination of this step is of considerable importance because phenylhydrazine is expensive and the filtration of *d*-gulose phenylhydrazone is frequently very slow. Since the new compound, α-*d*-gulose $CaCl_2 \cdot H_2O$, may be used directly for the preparation of many derivatives, it should now be possible to extend our knowledge of the chemistry of the gulose eries.[19]

[19] The author has prepared a number of crystalline derivatives of *d*-gulose from α -*d*-gulose $CaCl_2 \cdot H_2O$, hich will be reported in subsequent publications.

III. EXPERIMENTAL DETAILS

1. PREPARATION OF CRUDE *d*-GULOSE

The method which was used for the preparation of the cru *d*-gulose was essentially that of Fischer and Stahel.[20] Ninety gra gulonic lactone dissolved in 900 ml of water were placed in a 10-li pail and cooled to and maintained at 0° C. by an ice-salt mixtu Simultaneously small portions of 2 *N* sulphuric acid and 2.5 per ce sodium amalgam were added while the solution was vigorously stirr with a mechanical stirrer. The solution was held slightly acid (purp to congo red paper) by adjusting the rates at which the sodiu amalgam and sulphuric acid were added. A total of 2,000 g sodium amalgam were added which required about four hou When the sodium amalgam was exhausted as shown by the fact th the addition of sulphuric acid was no longer necessary to maint the desired acidity, the aqueous solution was decanted from t mercury and filtered. The filtrate was concentrated in vacuo t about 500 ml. It was then diluted with an equal volume of eth alcohol and the sodium sulphate was separated by filtration. Th filtrate was made definitely acid (blue to congo red paper) with 2 N sulphuric acid and then concentrated in vacuo to a thick sirup This sirup was diluted with an equal volume of methyl alcohol an seeded with gulonic lactone. After two days 25 g of crystalline gulon lactone were reclaimed. The alcohol was distilled from the moth liquor, which, after diluting slightly with water, was made alkalin (pink to phenolphthalein) with 2 *N* sodium hydroxide. Care wa taken to neutralize completely the remaining gulonic lactone. Afte the solution was adjusted to neutrality (colorless to phenolphthalein it was concentrated in vacuo to a thick sirup which was then poure into 10 volumes of hot 95 per cent ethyl alcohol. The alcoholi solution was decanted and the residue was thoroughly extracted wit several portions of hot 95 per cent alcohol. After evaporating th alcohol in vacuo, crude gulose sirup (40 g) was obtained which stil contained some inorganic salts, but which was suitable for the prep aration of gulose phenylhydrazone, or α-*d*-gulose $CaCl_2 \cdot H_2O$.

2. PURIFICATION OF CRUDE GULOSE BY ITS PHENYLHYDRAZONE

The sample of α-*d*-gulose $CaCl_2 \cdot H_2O$ which was used for the determination of its optical properties was prepared from a gulose sirup obtained from *d*-gulose phenylhydrazone by the method of Blanksma and van Ekenstein.[21]

Twenty grams of the crude gulose sirup were dissolved in 50 ml of water containing a few drops of acetic acid and then mixed with 12 g of phenylhydrazine. The reaction occurred quickly and a semisolid product resulted which was kept stirred until the reaction was complete. After about one hour the product was filtered by suction and washed with water. It was sucked as dry as possible and then washed with ether. The hydrazone is very soluble in dilute alcohol, but is readily recrystallized from absolute alcohol. About 18 g of recrystallized gulose phenylhydrazone were obtained. The phenylhydrazine was removed by refluxing 18 g of gulose phenyl-

[20] See footnote 5, p. 742.

[21] See footnote 6, p. 742.

hydrazone with 15 ml of benzaldehyde, 18 ml of alcohol, and 15 ml of water. The solution was filtered and the filtrate extracted several times with ether to remove the excess benzaldehyde and the benzaldehyde phenylhydrazone. After the addition of about 1 g of decolorizing carbon the solution was filtered and evaporated. Attempts were made in vain to bring the resulting colorless gulose sirup to crystallization.

PREPARATION OF α-d-GULOSE $CaCl_2 \cdot H_2O$ FROM THE GULOSE SIRUP OBTAINED FROM THE PHENYLHYDRAZONE

Twenty grams of thick gulose sirup prepared from *d*-gulose phenylhydrazone were mixed with a solution of 30 g of pure crystalline calcium chloride in 50 ml of water. The solution was evaporated under reduced pressure to a thick sirup, which, when allowed to stand in a desiccator over sulphuric acid, crystallized spontaneously. After several days the mixture was diluted with about 150 ml of absolute alcohol and the crystals (14 g) were separated by filtration. After concentration, a second crop of crystals (5 g) was obtained. The crystals are very difficultly soluble in hot ethyl alcohol and practically insoluble in ether and other similar organic solvents. The salt may be recrystallized by dissolving in a very small amount of hot water; on cooling, the crystals separate from the thick mother liquor which is diluted with absolute alcohol to facilitate filtration. A second crop of less pure gulose calcium chloride may be obtained by the addition of dry ether to the mother liquor. For analysis the product was recrystallized five times and dried to constant weight (18 hours) at 100° C. in vacuo. *Analysis calculated for* $C_6H_{12}O_6\ CaCl_2 \cdot H_2O$: C, 23.29; H, 4.57; Ca, 12.96; Cl, 22.94. *Found:* C, 23.25; H, 4.55; Ca, 12.99; Cl, 22.82. *Check sample found:* Ca, 12.99; Cl, 22.80. *Loss on drying two hours at 100° in vacuo:* Subs., 1.0725; loss, 0.0003. It decomposes with the evolution of gas and fusion at about 205° C.

4. OPTICAL ROTATION OF α-d-GULOSE

The determination of the optical rotation of α-*d*-gulose was conducted in a constant temperature room at 20° C. 1.2238 g of finely powdered α-*d*-gulose $CaCl_2 \cdot H_2O$ and 2 g of freshly prepared dry silver oxalate [22] were placed in a glass-stoppered flask and 24.9550 g of water were added from a pipette which had been calibrated and found to deliver that weight of water in 20 seconds. Preliminary experiments had shown that 1.2 g of finely powdered α-*d*-gulose $CaCl_2 \cdot H_2O$ could be dissolved in 25 ml of water in about 20 seconds. The time was measured from the moment when it was believed that half of the sugar was dissolved. This was about 5 seconds after the addition of the first water when about half of the water had drained from the pipette. The mean time when the mutarotation started is probably within 5 or 10 seconds of the time thus estimated. The flask containing the gulose calcium chloride and silver oxalate was shaken 2.5 minutes, then 0.2 g of decolorizing carbon (Norit) was added and the solution filtered. The rotation of the filtered solution was read in a 2 dm "Landolt inversion tube" with a Bates saccharimeter. Initially the rotation was changing about 0.5° S per minute;

[22] The silver oxalate was prepared from silver nitrate and slightly acidified (oxalic acid) sodium oxalate. It was dried at 40° in vacuo and protected from light.

consequently the error in the reading is relatively large (possibly 0.
S). The temperature of the solution was measured at interva
after 6, 13, 18, 25, 30, and 50 minutes the following temperatures we
observed: 19.9°, 20.0°, 20.1°, 20.15°, and 20.15°. After completi
the optical measurements qualitative tests were made on the soluti
for chlorides, calcium, and silver. The tests for chlorides and calci
were negative. A very faint opalescence was obtained with a drop
hydrochloric acid which indicated that a trace of a silver salt was
solution, but the amount was negligible. The density of the soluti
was determined with a picnometer which had a capacity of 10.6
ml at 20° C. It held 10.7876 g of the solution at 20° C. (weighted
air) which gives a density of 1.0095. From the molecular weigh
1.2238 g of α-*d*-gulose $CaCl_2 \cdot H_2O$ is equivalent to 0.7130 g of gulo
and 0.0713 g of H_2O. This water must be added to the water deliver
from the pipette (24.9550 g) because it is liberated when the calci
chloride is removed. Thus 0.7130 g of *d*-gulose was contained
25.0263 g of water, which gives 25.7393 g of solution. This is equiv
lent to 25.5 ml of a solution of 1.0095 density. The values given
Table 1 were then calculated as explained in the footnotes. It shou
be noted that all the calcium chloride was removed in less th
2.5 minutes after the addition of water and that the rates of mutar
tation of the $CaCl_2$ compound, and the gulose solution are sufficient
near to each other that the initial rotation may be extrapolated
zero time.

5. PREPARATION OF α-*d*-GULOSE $CaCl_2 \cdot H_2O$ FROM THE REDUCTIO PRODUCT OF GULONIC LACTONE

Twenty grams of the thick gulose sirup, which was prepared
given before [21] were mixed with a solution of 30 g of anhydrous calciu
chloride in 150 ml of 95 per cent ethyl alcohol. A small quantity
amorphous material was precipitated which was removed by filtr
tion. The clear filtrate was gently warmed and stirred. After a shor
time crystallization occurred. (The product usually crystalliz
spontaneously, although with impure sirups nucleation and concen
tration is necessary.) About 20 g of crystalline α-*d*-gulose $CaCl_2 \cdot$
H_2O were obtained. By concentrating the filtrate to 50 ml, an
saturating the sirup with ether, a second crop of crystals (8 g) wa
obtained. The final product, when prepared from sirups containin
sodium salts, usually contains some sodium chloride which is difficul
to remove. Hence, if one desires only a small quantity of a pur
product it is usually advisable to start with a pure gulose solution
such as is obtained from *d*-gulose phenylhydrazone. But if a larg
quantity of material is desired, especially if a small quantity of sodium
chloride is not objectionable, it is far easier to prepare it directly fro
the crude sirup.

IV. SUMMARY

A crystalline calcium chloride compound of α-*d*-gulose ($C_6H_{12}O_6 \cdot$
$CaCl_2 \cdot H_2O$) has been prepared, and its optical rotation studied. It
exhibits mutarotation: The extrapolated initial specific rotation
$[\alpha]_D^{20} = +37.7$; at equilibrium, $[\alpha]_D^{20} = -15.4° + 0.78\ C.$, where C is
the concentration of α-*d*-gulose $CaCl_2 \cdot H_2O$ in grams per 100 ml;
the mutarotation coefficient, $k_1 + k_2 = 0.0193$ at 20°C.

[21] See p. 752.

If the calcium chloride is removed from a freshly prepared solution of *α-d*-gulose $CaCl_2 \cdot H_2O$ by means of silver oxalate, the resulting solution of pure *α-d*-gulose shows a rate of mutarotation ($k_1+k_2=0.0206$) close to that given by *d*-gulose calcium chloride and near to that given by the closely related sugar *d*-mannose. The molecular rotation of *α-d*-gulose was found to be +11,100, which differs only slightly more than the probable error from the molecular rotation +11,650 of *α-d*-gulose $CaCl_2 \cdot H_2O$.

The equilibrium rotation of *d*-gulose in the absence of calcium chloride is not appreciably altered by small changes in the concentration of the sugar, but the equilibrium rotation of *d*-gulose $CaCl_2$. H_2O is greatly altered by small changes in the concentration of the compound. Concentrated solutions of the calcium chloride compound exhibit on dilution with water a mutarotation rate approximately equal to the mutarotation rate of *d*-gulose. This mutarotation shows that the salt changes the equilibrium rotation of *d*-gulose by altering in some manner the relative amounts of the different forms of the sugar in solution.

V. ACKNOWLEDGMENT

The author expresses his appreciation to F. P. Phelps, of this bureau, who kindly made the photograph given in Figure 1; to C. S. Hudson, who first suggested a study of this sugar; to R. F. Jackson and to other members of the polarimetry section, who have aided in the course of this investigation.

WASHINGTON, April 28, 1930.

NOTE ON THE ELECTRICAL RESISTANCE OF CONTACTS BETWEEN NUTS AND BOLTS

By Frank Wenner, G. W. Nusbaum, and B. C. Cruickshanks

ABSTRACT

Measurements were made of the electrical resistance between nuts and bolts, using two radically different types of threads, the American National and the Dardelet, and different materials. The test specimens were three-fourths inch bolts of copper, brass, bronze, and steel with nuts of the same materials. The resistances between nuts and bolts were measured with stresses in the bolts, applied by turning the nuts, in the range from near zero to well toward the elastic limit of the materials. It was found that the contact resistance is usually less than a 1-inch length of bolt and that under similar conditions the resistance of the Dardelet thread is, in general, not more than one-fourth that of the American National thread. The maximum resistances found were for steel bolts having the American National thread. For these with a stress of 2,000 lbs./in.^{2} in the bolts the resistance is about 10 microhms, which is the resistance of about an inch length of the bodies of the bolts. The minimum resistances found were for copper bolts having Dardelet threads. For these, with a stress of 6,000 or more lbs./in.^{2} in the bolts, the resistance is of the order of 0.02 microhm which is the resistance of about one sixty-fourth inch length of the bolts.

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I. INTRODUCTION

Every piece of electrical equipment requires some sort of connections between various parts of a circuit. To facilitate assembly, the connections are often made by means of bolts or machine screws. When the construction is such that the bolt and nut, or other threaded device forms a part of the electric circuit, the electrical resistance of such contacts is of more or less importance, depending upon the nature of the apparatus, and little, if any, definite information on the subject is available.

The purpose of this investigation was to measure the resistance of such contacts when made through different types of threads in different materials and with different stresses in the bolts or screws. The types of thread selected were the American National coarse thread and the Dardelet thread. The materials selected were steel, brass, bronze, and copper; and the stresses in the bolts ranged from near zero well up toward the elastic limit of the materials.

II. DESCRIPTION OF SCREW THREADS USED

The American National form of thread (formerly the United States Standard thread) is so well known that a description is unnecessary. A cross section of this thread is shown in Figure 1 and with the nut only in section in Figure 2.

The Dardelet thread is comparatively new so it will be described somewhat in detail. Figure 3 shows the nut in a position which it may take with no tension in the bolt. In this position the nut turns freely on the bolt. Figure 4 shows the nut in the position which it takes with the working tension in the bolt. In this position

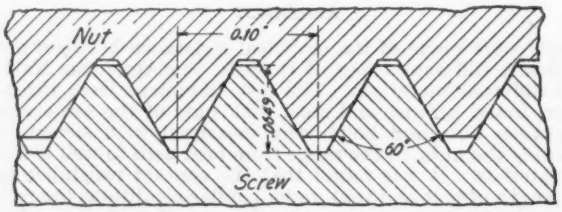

FIGURE 1.—*Section of the American National form of coarse thread, formerly known as the United States Standard thread*

the nut is locked to the bolt. The inclinations of the sides are the same as the Acme thread. The surfaces at the major diameters are cylindrical with clearance between the bolt and nut. The surfaces at the minor diameters are helical cones.

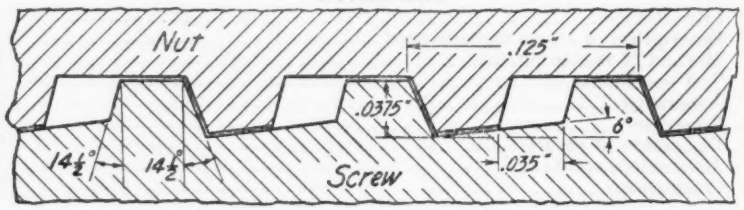

FIGURE 5.—*Detailed section of the Dardelet thread with nut in free position on the screw*

When the nut is screwed on the bolt, there is clearance between the threads of the two pieces, as shown in Figure 3 and also in Figure 5. When the nut is screwed down by hand into contact with the parts to be clamped, the helical cones come into contact. As the nut is turned to increase the tension in the bolt, the helical cones are

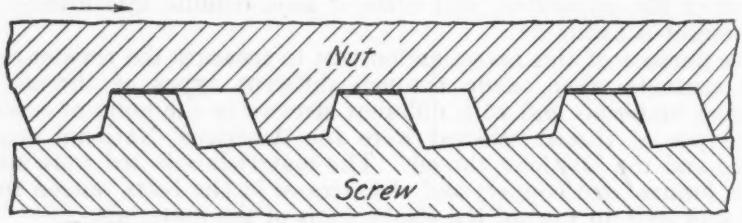

FIGURE 6.—*Detailed section of Dardelet thread with the locking cones compressed and the thrust faces in contact*

compressed elastically until the thrust faces come into contact as shown in Figures 4 and 6. The load on the bolt is then sustained largely by the thrust faces of the threads, and the tapered surfaces at the minor diameter of the threads are highly compressed. It is this close contact which resists the backing off of the nut, even though the tension in the bolt be released.

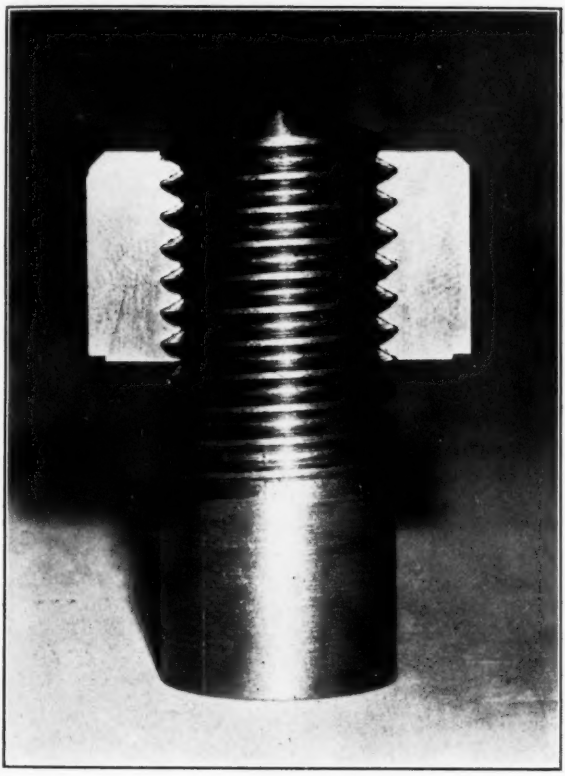

FIGURE 2.—*The American National form of coarse thread with nut only in section*

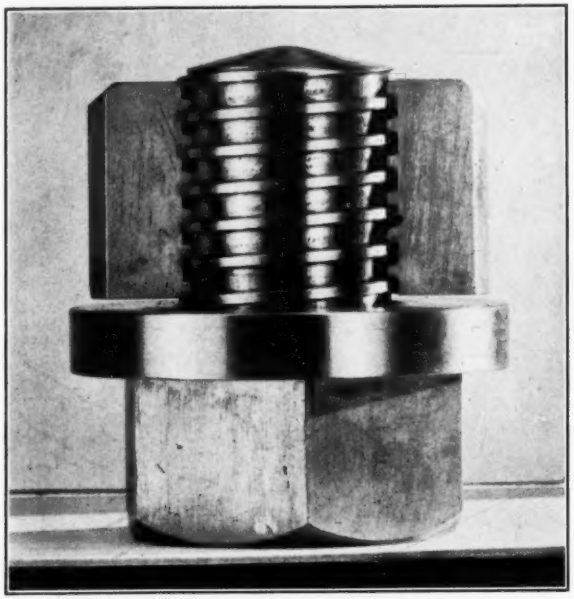

FIGURE 3.—*The Dardelet thread with the nut in position on the screw where it is free to turn*

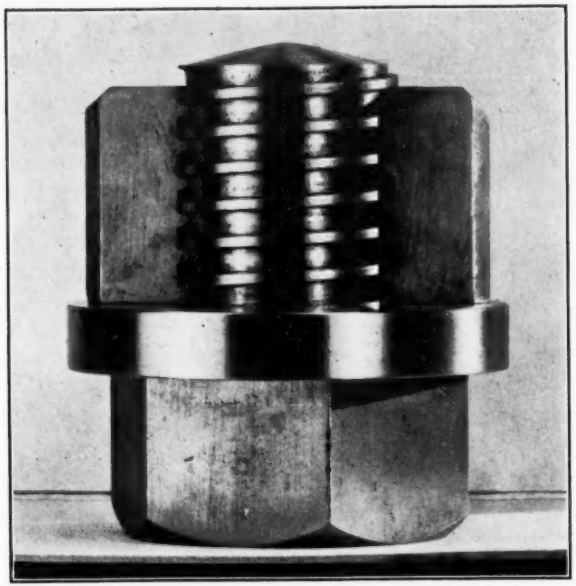

FIGURE 4.—*The Dardelet thread with thrust faces of nut and screw threads in contact*

This is the position of the nut on the bolt when the tension in the bolt is sufficient to compress the locking cones.

III. METHOD OF MEASUREMENT

The measurements were made by passing current from the nut to the bolt and comparing the drop in potential from the nut to the bolt with the drop in potential across a known resistance in the circuit. The comparisons were obtained from the relative deflections of a galvanometer when connected alternately to the nut and bolt and across the known resistance. The relative resistances were considered to have the same ratio as the relative deflections of the galvanometer when corrected for the different sensitivities which it was found necessary to use in order to include the wide range in values found. Precautions were taken to obtain an accuracy sufficient for the purpose.

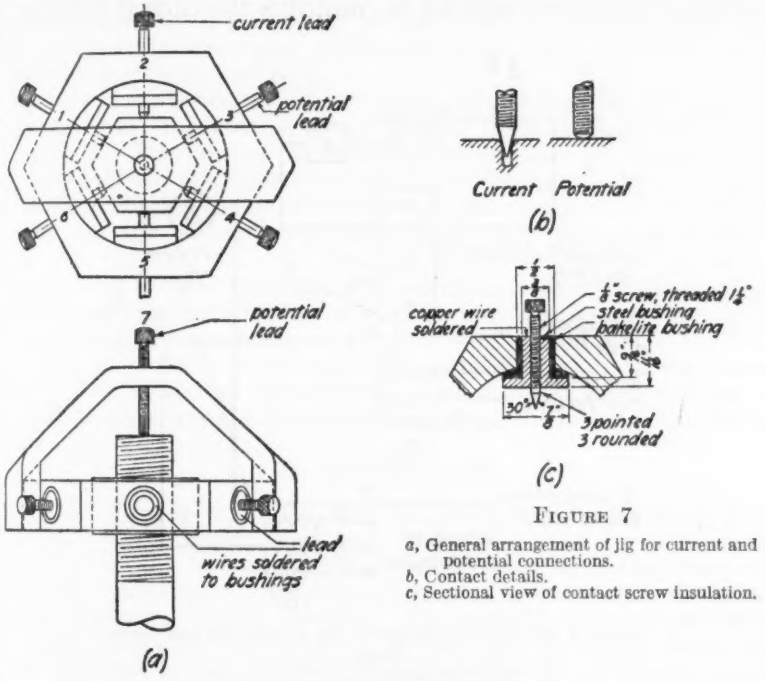

FIGURE 7

a, General arrangement of jig for current and potential connections.
b, Contact details.
c, Sectional view of contact screw insulation.

IV. TEST SPECIMENS

The bolts for the test specimens consisted of three-fourths inch rods of machine steel, brass, bronze, and copper. These were threaded in accordance with commercial practice, American National coarse threads at one end and Dardelet threads at the other. The nuts of steel, copper, and brass were all of the same size, thirteen-sixteenths inch thick and $1\frac{1}{16}$ inches across flats. The bronze nuts were thirteen-sixteenths inch thick and $1\frac{1}{8}$ inches across flats. The nuts, also, were threaded in accordance with commercial practice. In addition, there was one specimen of machine steel similar in shape to the other test specimens, but made from one piece so as to have no resistance between the part corresponding to the bolt and the part corresponding to the nut. This will hereafter be referred to as the one-piece specimen. Each nut had three holes drilled to a depth of slightly more than one-eighth inch and reamed, as shown in Figure 7 (*b*). These were

centered on alternate faces of the nut and served for definitely locating the electrical connnections.

V. APPARATUS

All electrical connections on the nuts were made by means of the jig shown in Figure 7 (*a*). Six radial screws entered steel bushings insulated, by bakelite bushings, from the body of the jig as shown in Figure 7 (*c*). Figure 7 (*b*) shows details of the screw contacts with the nut. Three screw points entered holes drilled in the three nonadjacent sides of the nut, and the other three screw ends made contact on the flat surfaces of the intermediate sides. The leads from screws *1*, *3*, and *5* were connected to conductors of equal resistance and these conductors connected together to constitute the current terminal for

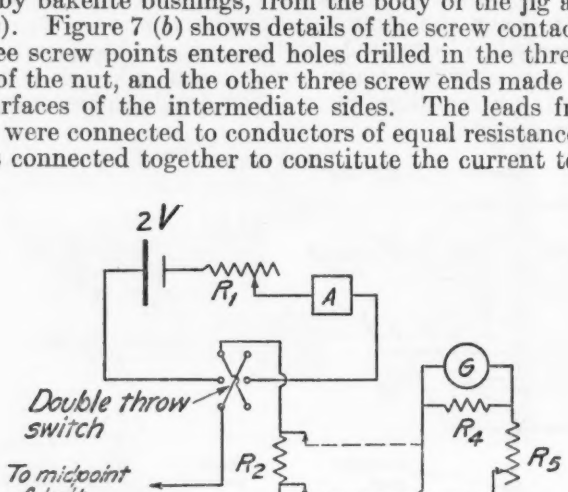

FIGURE 8.—*Wiring diagram for nut-to-bolt resistance tests*

the nut. The bolt current terminal (not shown) was made at the middle of the bolt. The leads from screws *2*, *4*, and *6* were connected to conductors of equal resistance, and these conductors connected together to constitute the nut potential terminal. Screw *7* constituted the bolt potential terminal. The use of branched current and potential terminals on the nut makes the resistance the same as the average which would be obtained from measurements made with the current connection first on one and then on another of the alternate faces of the nut, and for each of these three positions of the current terminal with the potential terminal first on one and then on another of the intermediate faces of the nut. Thus a single measurement gives the average of what would be obtained in nine separate measurements without branched current and potential terminals.

The arrangement of the electric circuit is shown in Figure 8. Here R_1 is an adjustable resistance for regulating the current; R_2 is a

constant resistance whose value was determined by comparison with a resistance standard and used as a reference standard; R_3 represents three conductors of equal resistance, one in each branch of the three-point current terminal to ensure a uniform distribution of the current between the three alternate faces of the nut; R_4 is a resistance used to properly damp the galvanometer; R_5 is an adjustable resistance for varying the sensitivity of the galvanometer; R_6 represents three conductors of equal resistance, one in each branch of the three-point potential terminal, to obtain the mean potential on the three faces of the nut between those faces on which the current is led into the nut. This arrangement constitutes a four-terminal resistance including the contact between the nut and bolt, but only a very small amount of the material of the specimen. The resistance of the material included was determined in a manner to be explained later and applied as a correction to the measured resistance to get the resistance of the contact between nut and bolt.

The test current was supplied by a two-volt storage cell and adjusted by means of the rheostat R_1 to the desired value, as indicated by the ammeter A. The double throw switch served for closing the circuit with the polarity of the battery in either direction. The resistance R_2 served to change the sensitivity of the galvanometer G, that is, the deflection of the galvanometer for a given potential drop in R_2, or across the nut and bolt, so that the deflections would be neither completely off the scale nor too small for reasonably accurate readings. A screw type testing machine served to measure the tension in the bolt, and a hand wrench served to apply this tension and at the same time slide the contact to simulate the usual procedure in the assembling of such electrical connections. The nut was supported on an insulated plate to avoid a short circuit through the frame of the testing machine.

VI. PROCEDURE

With the threads well oiled, the nut resting on the insulated plate supported by the upper head and the bolt gripped by jaws in the lower head of the testing machine, measurements of the resistance were made according to the method outlined above for each increment of stress (2,000 lbs./in.^{2}) in the bolt. The range of stresses used extended from practically zero to 16,000 lbs./in.^{2} for the copper, brass, and bronze specimens, and to 20,000 lbs./in.^{2} for the steel specimens. The stresses were calculated for a diameter corresponding to that at the root of the threads. To increase the load, it was necessary to remove temporarily the jig carrying the branched current and potential terminals. Measurements of the resistance were made only after an increase in the stress, except for the initial resistance. With the specimen merely placed in position, the resistance was found to be rather high and very indefinite. Before measuring the initial resistance the nut was turned with one hand while a downward pull was exerted on the bolt by the other hand. Then with the load reduced to merely the weight of the bolt, which was considered zero stress in the bolt, the resistance was found to be sufficiently definite to permit of measurement.

Two specimens of each of the four materials were used, and since each specimen had American National coarse threads on one end and Dardelet threads on the other, 16 sets of values were obtained.

The resistance of the one-piece specimen was measured with the same arrangement of current and potential terminals used in the measurements of the resistance between nut and bolt. The resistance of a 4-inch length of one bolt of each of the four materials was also measured, from which the relative conductiveness of the four materials could be found. In the latter measurements single-current leads were clamped near the ends of the bolt, while potential connections were made by means of knife-edges attached to a spacer of insulating material and pressed lightly against the side of the bolt. From the measured resistance of the one-piece specimen and the relative conductivities of the materials, the resistances of one-piece specimens of the other materials were calculated. The values for one-piece specimens found in this way were subtracted from the measured resistance of the nut and bolt specimens and the differences considered to be the resistances of the contacts between the nuts and bolts. The results obtained are given in Tables 1 to 4 and except for zero stress are shown graphically in Figures 9 and 10. Figure 9 gives the results for the two steel specimens plotted separately. This gives a fair idea of the agreement of the measurements on duplicate specimens. Figure 10 gives the resistances for all materials plotted to a different scale from that used in Figure 9 and here each point represents the average of the values obtained for the two specimens.

TABLE 1.—*Contact resistance between nut and bolt*

Stress in bolt	Contact resistance					
	American National thread			Dardelet thread		
	Steel specimen No. 1	Steel specimen No. 2	Average	Steel specimen No. 1	Steel specimen No. 2	Average
Lbs./in.²	*Microhms*	*Microhms*	*Microhms*	*Microhms*	*Microhms*	*Microhms*
0	300.4	301.9	301.2	353.4	49.7	201.5
2,000	7.48	9.31	8.40	1.21	1.34	1.28
4,000	3.96	5.47	4.72	.635	.82	.73
6,000	3.00	3.90	3.45	.402	.63	.52
8,000	2.40	3.26	2.83	.30	.47	.39
10,000	1.74	2.84	2.29	.25	.39	.32
12,000	1.45	2.30	1.88	.28	.28	.28
14,000	1.17	1.81	1.49	.21	.27	.24
16,000	.92	1.66	1.29	.22	.29	.25
18,000	.89	1.44	1.17	.18	.29	.24
20,000	.59	1.31	.95	.17	.22	.19

TABLE 2.—*Contact resistance between nut and bolt*

Stress in bolt	Contact resistance					
	American National thread			Dardelet thread		
	Bronze specimen No. 1	Bronze specimen No. 2	Average	Bronze specimen No. 1	Bronze specimen No. 2	Average
Lbs./in.²	*Microhms*	*Microhms*	*Microhms*	*Microhms*	*Microhms*	*Microhms*
0	28.17	61.57	44.87	17.59	31.77	24.68
2,000	1.34	1.69	1.51	.35	.45	.40
4,000	.86	.82	.84	.154	.186	.17
6,000	.60	.58	.59	.132	.127	.130
8,000	.45	.51	.48	.116	.127	.122
10,000	.33	.38	.355	.089	.100	.095
12,000	.31	.32	.315	.099	.110	.105
14,000	.239	.31	.274	.089	.110	.10
16,000	.239	.257	.248	.078	.100	.089

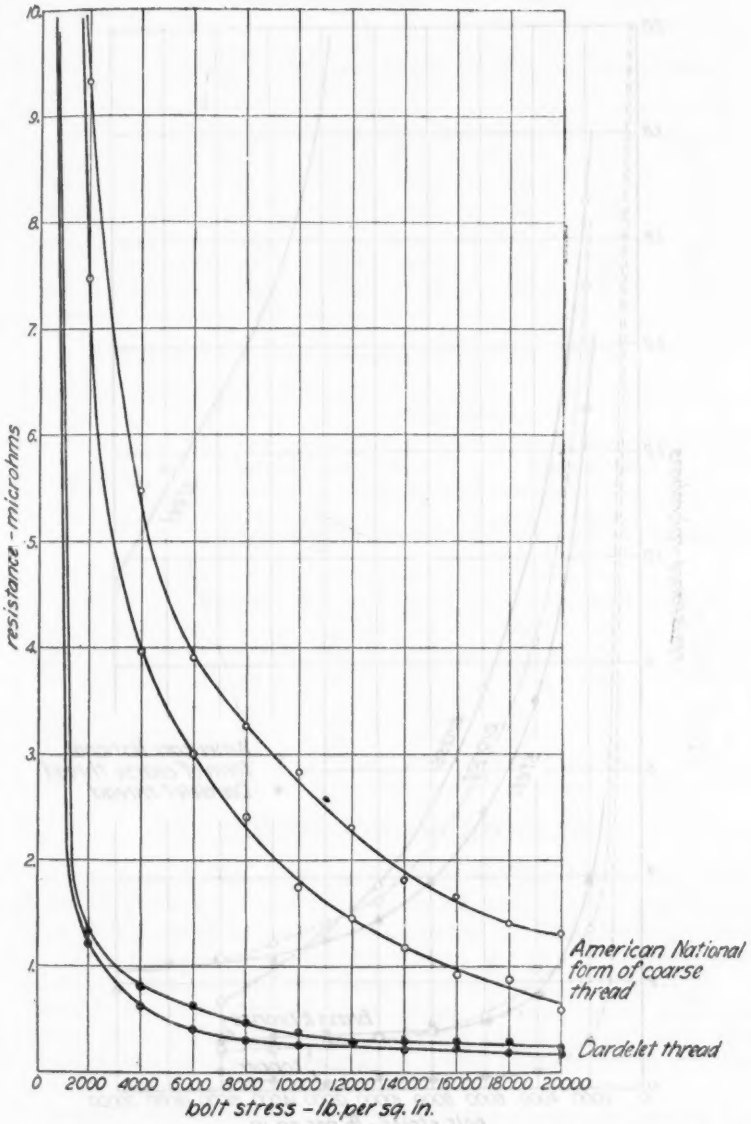

FIGURE 9.—*Nut-to-bolt resistance tests on steel (two specimens)*

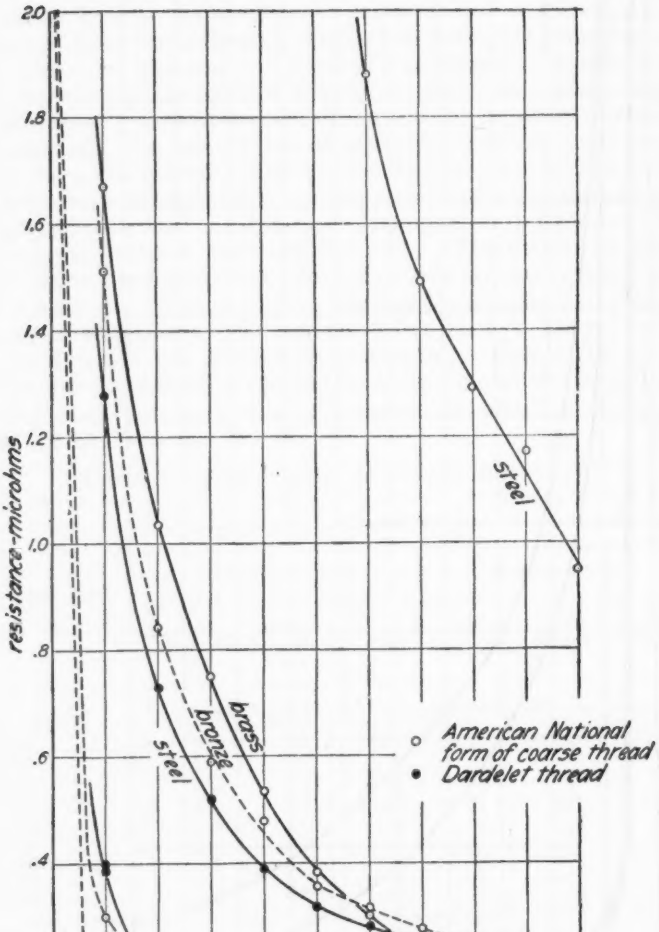

FIGURE 10.—*Nut-to-bolt resistance tests on copper, bronze, brass, and steel*

TABLE 3.—*Contact resistance between nut and bolt*

Stress in bolt	Contact resistance					
	American National thread			Dardelet thread		
	Brass specimen No. 1	Brass specimen No. 2	Average	Brass specimen No. 1	Brass specimen No. 2	Average
Lbs./in.²	*Michroms*	*Michroms*	*Michroms*	*Michroms*	*Michroms*	*Michroms*
0	55.18	11.18	33.18	12.78	15.08	13.93
2,000	1.45	1.89	1.67	.358	.42	.389
4,000	.74	1.33	1.04	.160	.18	.170
6,000	.53	.97	.75	.131	.131	.131
8,000	.34	.73	.535	.116	.116	.116
10,000	.244	.53	.387	.101	.096	.099
12,000	.228	.373	.301	.101	.067	.084
14,000	.18	.254	.217	.096	.081	.089
16,000	.142	.195	.169	.086	.06	.073

TABLE 4.—*Contact resistance between nut and bolt*

Stress in bolt	Contact resistance					
	American National thread			Dardelet thread		
	Copper specimen No. 1	Copper specimen No. 2	Average	Copper specimen No. 1	Copper specimen No. 2	Average
Lbs./in.²	*Michroms*	*Michroms*	*Michroms*	*Michroms*	*Michroms*	*Michroms*
0	24.9	9.3	17.1	1.67	2.91	2.29
2,000	.27	.33	.30	.084	.093	.088
4,000	.24	.21	.225	.036	.029	.033
6,000	.127	.141	.134	.036	.007	.022
8,000	.108	.104	.106	.021	.002	.012
10,000	.093	.093	.093	.021	.023	.022
12,000	.074	.093	.083	.011	.007	.009
14,000	.069	.088	.078	.011	.018	.015
16,000	.060	.098	.079	.036	.029	.033

VII. DISCUSSION OF RESULTS

For stresses of 2,000 or more lbs./in.² in the bolts, the contact resistance between nuts and bolts is small, and that of the Dardelet thread is much smaller than that of the American National coarse thread. The highest resistance shown on the graph corresponds to the resistance of about an inch length of the body of the bolt.

It should be remembered that these threads were well oiled. Experience with different types of sliding electrical contacts shows that usually the electrical resistance when oiled is about one-tenth the electrical resistance when dry.

The contact resistance is lower with those materials having lower electrical resistivity; that is, having higher electrical conductivity. However, for otherwise similar conditions all of the observed differences in the contact resistance can not be accounted for on this basis.

We have defined the contact resistance as the difference in the electrical resistance of two specimens of the same material and dimensions, one being solid and the other consisting of two pieces (nut and

bolt). The idle faces and parts of the tops and bottoms of the threads can not be in electrical contact. Further, since these nuts and bolts had threads of commercial quality, with somewhat rough surfaces as may be seen by reference to Figures 2, 3, and 4, all of that part of the surface supporting the load may not have been in electrical contact. However, with the same load the area in contact was, no doubt, greater in the case of the softer materials than in the case of the steel and greater with Dardelet than with American National threads. As the stress in the bolt was increased by turning the nut, it is easily understood that the area in electrical contact would be increased even to the point of being equal to that of the supporting surface if the stress could be made sufficiently great. This is at least a logical explanation as to why the contact resistance is lower with soft than with hard materials, lower with Dardelet than with American National threads, and tends toward a minimum rather than a zero value as the stress in the bolts is increased.

The extent to which the results given in this paper would apply under radically different conditions can not be estimated.

VIII. ACKNOWLEDGMENTS

The authors wish to express their appreciation and thanks to Prof. H. L. Whittemore, chief of the engineering mechanics section, and to Dr. L. B. Tuckerman, assistant chief of mechanics and sound division, both of the Bureau of Standards, for their cooperation in this investigation.

IX. CONCLUSIONS

1. The electrical contact resistance (between nut and bolt) decreases as the stress in the bolt increases and becomes nearly constant as the stress approaches the yield point of the material.

2. For bolts of the same size and material under equal stresses in the bolt, the contact resistance (between nut and bolt) of the American National coarse thread is, in general, more than four times the corresponding resistance of the Dardelet thread.

3. With oiled Dardelet threads on three-fourths-inch bolts under stresses of 4,000 or more lbs./in.^{2}, applied by turning the nuts on the bolts, the contact resistances between nuts and bolts are less than the resistances of an one-eighth inch length of the bodies of the bolts.

WASHINGTON, June 20, 1930.

RP228

ADDITION AGENTS IN COPPER ELECTROTYPING SOLUTIONS

By R. O. Hull[1] and W. Blum

ABSTRACT

The effects of various addition agents in copper electrotyping solutions were investigated. It was found that phenol in the form of phenolsulphonic acid is most satisfactory. Its use permits the electrotypes to be produced in much shorter time, and to be harder than those obtained in ordinary baths.

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I. INTRODUCTION

Many "addition agents" have been proposed for copper deposition, though comparatively few have been employed on a commercial scale. Of the latter, glue is the best known and is used almost universally in copper refining. In electrotyping, the conditions for copper deposition are quite different from those used in refining. This research[2] represents a brief survey of the effects of a few typical addition agents in copper electrotyping baths, and the definition of the most favorable operating conditions for baths containing phenolsulphonic acid, which appears to be the most promising of the additions tried.

No attempt will be made in this paper to furnish details for the operation of electrotyping solutions. Such information will be included in a forthcoming revision of Bureau of Standards Circular No. 52.

[1] Research associate, International Association of Electrotypers.

[2] The experimental part of this research was conducted by R. O. Hull, employed as a research associate by the International Association of Electrotypers.

II. FUNCTIONS AND REQUIREMENTS OF ADDITION AGENTS IN ELECTROTYPING SOLUTIONS

In most cases an addition agent is introduced into a depositing bath in order to produce smoother deposits at a given current density or to permit higher current densities to be used in the production of equally smooth deposits. In electrorefining and electroplating, smoothness of deposits is more important than in electrotyping. Slight roughness on the back of an electrotype shell is actually advantageous, as it leads to better adherence of the type metal used to "back up" the copper.

In general, as the current density is increased, there is a tendency for the deposit to become rougher. A further increase in current density causes the deposit to become "burnt"; that is, dark and spongy. The latter condition may result from a depletion of metal ions in the cathode film or an increase in the pH of the latter. In either case basic compounds are likely to be included in the deposit. Whether the permissible rate of deposition will be determined by the appearance of roughness or of burning will depend largely on the requirements of the product.

Practical experience and research have shown that higher current densities can be used without causing burning if a high concentration of metal ions is maintained in the cathode film. The factors that favor this condition include (*a*) a high concentration of the metal salt, in this case copper sulphate, (*b*) a high temperature, and (*c*) good agitation. However, these conditions produce relatively soft copper deposits. In actual practice, therefore, the principal purpose of addition agents in electrotyping is to produce harder copper deposits than are obtainable under conditions otherwise favorable for rapid deposition. Addition agents do not as a rule overcome burning of deposits; in fact, in many cases they reduce the limiting current density below that which can be used in similar solutions containing no addition agent.

While meeting the above purpose, it is desirable that an addition agent for use in electrotyping should not need close control, as electrotyping is usually carried out in relatively small plants, without the aid of chemical analysis. It is therefore preferable to use a substance that is effective over a wide range of concentrations and that does not require frequent replenishment. The cost of the addition agent is less significant than in refining, which is carried out on a much larger scale.

III. FAVORABLE CONDITIONS FOR OPERATION WITHOUT ADDITION AGENTS

As noted above, the principal function of addition agents in electrotyping is to counteract the tendency to produce soft copper deposits under the conditions that are otherwise favorable for rapid deposition. The first part of this investigation involved a brief study of the conditions for rapid copper deposition from solutions containing only copper sulphate and sulphuric acid.

The chief function of the copper sulphate is to furnish the metal ions required for deposition. The sulphuric acid greatly increases the conductivity, an effect which is especially important when high-current

nsities must be obtained with a limited voltage. (Most generators d in electroplating and electrotyping furnish current at 6 volts. nerators with two commutators will supply current at 12 volts th, however, a corresponding decrease in their current capacity.) addition, the sulphuric acid reduces anode polarization and thereby reases the anode efficiency. It also retards the formation of burnt posits.

On general principles it might, therefore, be assumed that the ncentrations of both copper sulphate and sulphuric acid should be de as high as possible. But the addition of sulphuric acid reduces e solubility of copper sulphate; hence it is necessary to select the mbination which most nearly meets the requirements of metal and drogen ion concentration and conductivity.

In determining the optimum conditions of deposition, the copper s deposited upon thin sheet lead (about 10 by 15 cm or 4 by 6 ches) that had been treated with a dilute chromate solution to rmit subsequent separation of the copper sheets. The lead was ld in a hard rubber frame and so placed in a glass battery jar that th the current density and the agitation were nearly uniform over e entire cathode surface. The agitation was produced between e anode and cathode by introducing air through small holes in a ass tube. The rolled copper anode had approximately the same ea as the cathode and was placed about 10 cm (4 inches) from the tter. The temperature was kept within 1° C. of that desired, by mmersing the vessel in a water bath at an appropriate temperature.

Numerous experiments, of which the details are unimportant, owed that fairly smooth but soft copper deposits can be obtained pidly under conditions such as the following:

1. COMPOSITION OF THE SOLUTION

	Approximately normal	g/l	Avoirdupois oz./gal.
pper sulphate, $CuSO_4.5H_2O$	2	250	33
phuric acid, H_2SO_4	1.5	75	10

2. TEMPERATURE

40° C. or 104° F. (This is about the maximum temperature that n be safely used without softening the wax molds employed in elec- otyping.)

3. AGITATION

As good and as uniform as can be produced by introducing air rough suitable pipes.

4. CURRENT DENSITY

Under these conditions, a current density of 25 amp/dm^2 (230 amp/ ^{2}) can be used. This generally requires in practice a potential of least 6 volts at the tank. When this is not available, or when the itation is not the best, the current density may have to be reduced, r example, to 15 amp/dm^2 or 140 amp/ft.^{2}

5. TIME REQUIRED

The deposition of the ordinary electrotype shell with an average thicknes of 0.15 mm or 0.006 inches requires about 13 ampere-hours per dm^2 or 120 ampere-hours per square foot. At the maximum current density suggested above, about one-half hour will be required to deposit the shell, and a correspondingly longer time when lower current densities are employed. When no addition agents are present it is customary in commercial plants to use a current density of only about 7 amp/dm^2 (65 amp/$ft.^2$) and to take about two hours for the deposition. If, therefore, by means of addition agents, suitably hard deposits can be produced in a shorter time, it will be a great advantage, especially in periods of peak production, or for rush orders.

IV. EFFECTS OF ADDITION AGENTS

Preliminary tests were made in a bath of the above composition with several typical additions that have been used or suggested for copper baths, including glue, dextrin, urea, and phenol. These produced the following effects.

1. GLUE

Glue had the most marked effect of any addition agent tried. Under the most favorable conditions with high current densities it produced very smooth, hard deposits. The optimum concentration was found to be about 10 mg/l (0.0013 oz./gal.), which is over three times the concentration commonly used in copper refining, in which there is no air agitation and in which a relatively low current density is employed (about 2 amp/dm^2 or 19 amp/$ft.^2$). The concentration of glue must be kept within fairly close limits to be effective. A smaller concentration than the above has very little effect at these high current densities, while a much higher content of glue leads to the production of brittle deposits. There is no method of determining this small content of glue by analysis. Its estimation by measuring the polarization, as suggested by H. E. Haring [3] for copper refining baths, is not applicable, as the maximum polarization is reached with about 10 mg/l of glue. Although glue is being employed successfully in a few electrotyping plants, it is not well suited for this purpose.

2. DEXTRIN

Dextrin in a concentration of 1 g/l (0.13 oz./gal.) produced deposits that were only slightly smoother than those from plain solutions. When the concentration was increased to 10 g/l (1.3 oz./gal.) the deposits were very smooth, but relatively soft. There was no increase in hardness of the deposits produced after continued electrolysis. Dextrin appears to have no special advantage to warrant its use in electrotyping.

3. UREA

A solution containing about 1 g/l (0.13 oz./gal.) of urea first yielded a deposit that was smooth, but soft and coarsely crystalline. After electrolysis for several hours the deposit then produced was hard and fine grained. It is evident that any effectiveness of urea as an addi-

[3] Trans. Am. Electrochem. Soc., 49, p. 417; 1926.

tion agent depends upon the formation from it of some substance of different properties. No attempt was made to identify this secondary product, as it in turn was apparently unstable. Within a few days the solution ceased to yield smooth or hard deposits. Similar results were obtained with a solution containing about 5 g/l (0.67 oz./gal.) of urea. While urea has been used to some extent commercially, it requires frequent replenishment and is not, therefore, especially suitable for electrotyping.

4. PHENOL

When phenol (1 g/l or 0.13 oz./gal.) was added directly to the solution, the deposit first produced was very soft and coarsely crystalline. When the electrolysis was continued for several hours, the deposits then produced were smooth, hard, and fine grained. Here again, it was evident that some product formed from the phenol was more effective than the phenol itself. The most obvious assumption was that the phenol had reacted slowly with the sulphuric acid to form phenolsulphonic acid. Upon this assumption the latter compound was prepared by heating equal volumes of phenol and concentrated sulphuric acid to 100° C. (212° F.) for one hour. The product was then introduced into a fresh solution in the amount necessary to yield the same concentration of phenol as was used above. Smooth, hard deposits were then obtained in the first electrolysis. This result indicated that it was preferable to add the phenol as phenolsulphonic acid in order to immediately get beneficial results. Another advantage in using the combined phenol is that in this form it is less readily volatilized from the agitated solution. Such volatilization causes a loss of phenol and also a disagreeable odor.

Continued tests with solutions containing phenolsulphonic acid showed that while an immediate beneficial effect was observed, the maximum effect was not obtained until after electrolysis for a few days. During this period the solution acquired a dark-green color, evidently produced by an optical combination of the blue of copper sulphate and some yellow or brown compound formed during electrolysis.

Because the solutions are agitated with air, conditions are favorable for the oxidation of any organic compounds that may be present. Among the products of oxidation of phenol are hydroquinol and quinone. Attempts to identify either of these compounds in the used solutions were not conclusive. However, when one of these substances was substituted for the phenolsulphonic acid the solution soon darkened and yielded smooth, hard deposits. It is probable that one (or both) of these compounds is formed in the solution to which phenolsulphonic acid has been added, and thus accounts for at least part of the observed effect.

If so, it might be added instead of the phenolsulphonic acid. Hydroquinol is relatively cheap and its use might be warranted in order to avoid the trouble and inconvenience of preparing the phenolsulphonic acid. It was subsequently tried in a few plant tests, but for some reason it did not yield as satisfactory results as did the phenolsulphonic acid. Quinone is relatively expensive, and its commercial use is probably not justified. A few experiments indicated that if the hydroquinol is first treated with acidified dichromate to oxidize it to quinone and the resulting solution is added to the bath, favorable results are obtained.

V. PLANT TESTS WITH PHENOLSULPHONIC ACID

As the laboratory experiments showed that phenolsulphonic acid is useful over a fairly wide range of concentration and that its effects are quite lasting, tests were made with it in several commercial electrotyping plants. These tests showed that by its use hard, smooth copper deposits can be produced without special precautions at much higher current densities than can otherwise be employed. In connection with these tests, analyses of the solutions were made at intervals in order to determine the rate of depletion of the phenolsulphonic acid and the effects of such depletion.

The result of the analysis was expressed as the total phenol equivalent. This included free phenol, that combined as the sulphonic acid and any hydroquinol or quinone formed in the bath. The method for determining phenol depends upon the fact that free bromine combines with phenol or its sulphonic acid to form tribromphenol

$$C_6H_5OH + 3Br_2 = .C_6H_2Br_3OH + 3HBr$$

Under similar conditions hydroquinol and quinone probably form bromine addition compounds. If these substances are present in considerable amount, the analytical result, expressed as "equivalent phenol," is only a rough guide to the total concentration of addition agent present.

The method was applied to the analysis of the copper bath as follows. Dilute a 10 ml sample of the solution to 50 ml and add 2 g of 20-mesh granulated zinc to precipitate the copper. When the copper is all removed, filter the solution into a 200 ml flask, and add 10 ml of a 0.1 *N* "bromine solution" and 50 ml of concentrated hydrochloric acid. (The bromine solution contains 2.8 g/l of potassium bromate and 12 g/l of potassium bromide. It is standardized against 0.1 N thiosulphate under the same conditions as are used for the determination.) Close the flask with a rubber stopper, and heat it in a water bath to 50° C. for one-half hour. Cool, add 2 ml of a 10 per cent solution of potassium iodide, shake well, and titrate the liberated iodine (using starch indicator) with 0.1 *N* thiosulphate, which has been similarly standardized against 0.1 *N* dichromate (4.9 g/l $K_2Cr_2O_7$). From the volumes of thiosulphate used in this titration and in the standardization of the bromine solution, the phenol equivalent of the solution may be calculated. One ml of 0.1 *N* bromine solution is equivalent to 0.00157 g of phenol.

Tests in several plants showed that after an initial rapid decrease the average depletion of phenol became less than 1 per cent per day. Decidedly beneficial results were obtained in one bath over a period of nearly six months, at the end of which period the deposits began to be soft and rough. During this time the equivalent phenol concentration, as determined by the above method, decreased from 1.0 g/l to 0.1 g/l. An addition of phenolsulphonic acid was then made to bring the concentration back to 1.0 g/l, and the deposits immediately became smooth and hard.

VI. CONCLUSIONS

While phenolsulphonic acid produces no beneficial effects upon the character of the copper deposits that might not be obtained with other addition agents in appropriate concentration, it appears better adapted for electrotyping than other substances. It is effective over a wide range of concentration and its effects (or those caused by products derived from it) persist over a long period of operation. The following conditions will probably be satisfactory for most electrotyping plants.

Suggested operating conditions

1. SOLUTION—	*N*	g/l	Averdupois oz./gal.
Copper sulphate, $CuSO_4.5H_2O$	2	250	33
Sulphuric acid, H_2SO_4	1. 5	75	10
Phenol (introduced as phenolsulphonic acid)		1	0. 13

2. TEMPERATURE—35° to 40° C. (95° to 104° F.).

3. CURRENT DENSITY—	amp/dm²	amp/ft.²
1. With very good agitation	25 to 30	230 to 280
2. With fair agitation or at lower temperature	10 to 20	90 to 180

The authors are indebted to N. Bekkedahl, who succeeded R. O. Hull as research associate and completed the plant tests and analyses; also to the officers and members of the International Association of Electrotypers for their cooperation and advice, especially in the plant tests.

WASHINGTON, May 1, 1930.

TERMS OF THE ARC AND SPARK SPECTRA OF CHROMIUM

By C. C. Kiess

ABSTRACT

Tables of terms are presented for the arc and first spark spectra of chromium. Babcock's unpublished Zeeman effects have aided in establishing many of them. Combinations of these terms account for nearly all the stronger lines of Cr I and Cr II. All the terms which have been identified conform to the requirements of Hund's theory.

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I. INTRODUCTION

The terms of Cr I and Cr II, presented herewith in Tables 1 and 2, are published at this time in response to numerous requests which have been made of the National Bureau of Standards for the classifications of the more prominent lines in the arc and spark spectra of chromium. The analyses of these spectra have been in progress at various times during the past decade at the bureau and elsewhere, and although the task is by no means completed, yet the terms already identified account for nearly all the strong lines of these spectra which are likely to be of interest to astronomers, physicists, and chemists.

The classifications made at the bureau have been greatly facilitated by new measurements of wave lengths in the arc and spark spectra, by King's temperature classifications,[1] and by Babcock's unpublished Zeeman effects, kindly placed at our disposal by him for this work. The terms of Cr I (Table 1), belong to the septet, quintet, and triplet systems and include those already published.[2] The terms of Cr II, and classifications based on them, belong to the sextet, quartet, and doublet systems. They have been partially described in previous communications and publications,[3] from which it would be possible to derive nearly all that have been found thus far. But for convenience they are now brought together in Table 2. Many of them have been confirmed by Krömer from an investigation of the Zeeman effect of Cr^+ at Tübingen. However, the term proposed by him for z^6D° is undoubtedly erroneous; and the pair of lines at 3291.76 and 3369.06 A,

[1] Astrophys. J., **41**, p. 167; 1915; **60**, p. 282; 1924.
[2] Kiess and Kiess, Science, **56**, p. 666; 1922. Catalán, Phil. Trans. Roy. Soc., **A 223**, p. 163; 1922; Anales Soc. Españ. Fis. Quim., **21**, p. 84; 1923. Gieseler, Ann. der Physik, **69**, p. 147; 1922; Zeit. für Physik, **22**, p. 228; 1924. Zumstein, Phys. Rev., **27**, p. 565; 1926. St. John, Revision of Rowland's Preliminary Table, p. 228; 1928. Ruark and Urey, Atoms, Molecules and Quanta, pp. 302-312; McGraw-Hill, New York, 1930.
[3] Meggers, Kiess, and Walters, J. Opt. Soc. Am. and Rev. Sci. Inst., **9**, p. 355; 1924. Kiess, J. Opt. Soc. Am. and Rev. Sci. Inst., **10**, p. 287; 1925. Kiess and Laporte, Science, **63**, p. 234; 1926. St. John, Revision of Rowland's Preliminary Table, p. 229; 1928. Dunham and Moore, Astrophys. J., **68**, p. 37; 1928. Krömer, Zeit. für Physik, **52**, p. 531; 1928. Dunham, Contrib. Princeton Univ. Observatory, No. 9; 1929.

regarded by him as emitted by the trebly ionized Cr atom, are accounted for by the doublet terms given below. Quite recently Catalán [4] has published a partial analysis of Cr II, his terms agreeing for the most part with those given below. The symbols used in designating the terms are those recently proposed as standard by Russell, Shenstone, and Turner.[5]

According to present theories of atomic structure the terms which characterize a spectrum represent the resultants of the interaction of the electrons outside the closed shells. Hund's theory [6] specifies these terms as to number and type for any particular electron configuration. The low and metastable terms of Cr I result from the configurations d^5s and d^4s^2. All the septet and quintet terms which arise from these electron groups have been found except ^5F. Of the triplet terms a few have been found but have not yet been connected with the quintets through intersystem combinations. No singlets have been established thus far. The configurations d^5, d^4s, and d^3s^2 give the low and metastable terms of Cr II. All the sextet and most of the quartet terms possible from these configurations are given in Table 2. Of the doublet terms only a few have been found. The higher terms which arise in both spectra, when an electron is dislodged to a p orbit, have been only incompletely identified. As stated above, however, the terms which have been established account for nearly all the stronger lines of the spectra and should serve to classify those lines of Cr I and Cr II which are likely to be of astrophysical and spectrochemical importance. Further discussion of the terms and their interpretation will be deferred until the complete classifications of the spectra are presented in subsequent papers.

II. TABLES OF TERMS OF Cr I AND Cr II

TABLE 1.—*Terms of Cr I*

Term	ν	$\Delta\nu$	Term	ν	$\Delta\nu$
a^7S_3	0. 0		a^5S_2	7, 593. 1	
e^7S_3	36, 895. 8		e^5S_2	37, 883. 1	
			f^5S_2	45, 967. 7	
e^7D_5	42, 261. 3				
e^7D_4	42, 258. 4	2. 9	a^5P_3	21, 840. 7	
e^7D_3	42, 256. 2	2. 2	a^5P_2	21, 847. 9	−7. 2
e^7D_2	42, 254. 5	1. 7	a^5P_1	21, 857. 0	−9. 1
e^7D_1	42, 253. 3	1. 2			
			a^5D_4	8, 307. 5	212. 3
f^7D_5	46, 959. 1		a^5D_3	8, 095. 2	167. 8
f^7D_4	46, 782. 9	176. 2	a^5D_2	7, 927. 4	116. 7
f^7D_3	46, 637. 2	145. 7	a^5D_1	7, 810. 7	60. 0
f^7D_2	46, 524. 9	112. 3	a^5D_0	7, 750. 7	
f^7D_1	46, 448. 6	76. 3			
			b^5D_4	24, 282. 3	−21. 6
g^7D_5	47, 709. 8		b^5D_3	24, 303. 9	+4. 1
g^7D_4	47, 705. 3	4. 5	b^5D_2	24, 299. 8	13. 2
g^7D_3	47, 702. 5	2. 9	b^5D_1	24, 286. 6	9. 5
g^7D_2	47, 700. 6	1. 8	b^5D_0	24, 277. 1	
g^7D_1	47, 699. 2	1. 4			

[4] Anales. Soc. Españ. Fis. Quim., **28**, p. 611; 1930.
[5] Phys. Rev., **33**, p. 900; 1929.
[6] Linienspektren und periodisches System der Elemente; Julius Springer, Berlin; 1927.

TABLE 1.—*Terms of Cr I*—Continued

Term	ν	$\Delta\nu$	Term	ν	$\Delta\nu$
e^5D_4	48, 824. 3	162. 9	$t^5P_3^\circ$	?	
e^5D_3	48, 661. 4	102. 9	$t^5P_2^\circ$	49, 598. 0	?
e^5D_2	48, 558. 5		$t^5P_1^\circ$	49, 588. 8	9. 2
e^5D_1	?				
e^5D_0	?		$s^5P_3^\circ$	49, 812. 3	
			$s^5P_2^\circ$	49, 822. 5	−10. 2
a^5G_6	20, 519. 3		$s^5P_1^\circ$	?	?
a^5G_5	20, 523. 8	−4. 5			
a^5G_4	20, 523. 6	+0. 2	$z^5D_4^\circ$	33, 816. 0	
a^5G_3	20, 521. 0	2. 6	$z^5D_3^\circ$	33, 671. 4	144. 6
a^5G_2	20, 517. 5	3. 5	$z^5D_2^\circ$	33, 542. 0	129. 4
			$z^5D_1^\circ$	33, 423. 6	118. 4
$z^7P_4^\circ$	23, 498. 9		$z^5D_0^\circ$	33, 337. 6	86. 0
$z^7P_3^\circ$	23, 386. 4	112. 5			
$z^7P_2^\circ$	23, 305. 0	81. 4	$y^5D_4^\circ$	41, 782. 2	
			$y^5D_3^\circ$	41, 575. 2	207. 0
$y^7P_4^\circ$	27, 935. 3		$y^5D_2^\circ$	41, 408. 9	166. 3
$y^7P_3^\circ$	27, 820. 3	115. 0	$y^5D_1^\circ$	41, 289. 2	119. 7
$y^7P_2^\circ$	27, 728. 9	91. 4	$y^5D_0^\circ$	41, 124. 7	164. 5
$x^7P_4^\circ$	42, 277. 0		$x^5D_4^\circ$	42, 908. 4	
$x^7P_3^\circ$	42, 251. 9	25. 1	$x^5D_3^\circ$	42, 648. 4	260. 0
$x^7P_2^\circ$	42, 237. 0	14. 9	$x^5D_2^\circ$	42, 438. 8	209. 6
			$x^5D_1^\circ$	42, 292. 8	146. 0
$z^7D_5^\circ$	27, 825. 2		$x^5D_0^\circ$	42, 218. 3	74. 5
$z^7D_4^\circ$	27, 649. 7	175. 5			
$z^7D_3^\circ$	27, 500. 3	149. 4	$w^5D_4^\circ$	47, 866. 4	
$z^7D_2^\circ$	27, 382. 1	118. 2	$w^5D_3^\circ$	47, 814. 3	52. 1
$z^7D_1^\circ$	27, 300. 3	81. 8	$w^5D_2^\circ$	47, 786. 1	28. 2
			$w^5D_1^\circ$	47, 772. 4	13. 7
$z^7F_6^\circ$	25, 771. 5		$w^5D_0^\circ$	47, 788. 1	−15. 7
$z^7F_5^\circ$	25, 548. 6	222. 9			
$z^7F_4^\circ$	25, 359. 6	189. 0	$v^5D_4^\circ$	50, 557. 5	
$z^7F_3^\circ$	25, 206. 0	153. 6	$v^5D_3^\circ$	50, 628. 1	−70. 6
$z^7F_2^\circ$	25, 089. 2	116. 8	$v^5D_2^\circ$	50, 654. 7	−26. 6
$z^7F_1^\circ$	25, 010. 7	78. 5	$v^5D_1^\circ$	50, 662. 9	−8. 2
$z^7F_0^\circ$	24, 971. 1	39. 6	$v^5D_0^\circ$	50, 661. 2	+1. 7
$z^5P_3^\circ$	26, 787. 3		$u^5D_4^\circ$	52, 064. 6	
$z^5P_2^\circ$	26, 796. 1	−8. 8	$u^5D_3^\circ$	52, 031. 9	32. 7
$z^5P_1^\circ$	26, 801. 8	−5. 7	$u^5D_2^\circ$	52, 012. 8	19. 1
			$u^5D_1^\circ$	52, 003. 7	9. 1
$y^5P_3^\circ$	29, 824. 7		$u^5D_0^\circ$	52, 000. 5	3. 2
$y^5P_2^\circ$	29, 584. 5	240. 2			
$y^5P_1^\circ$	29, 420. 7	163. 8	$z^5F_5^\circ$	31, 280. 0	
			$z^5F_4^\circ$	31, 106. 2	173. 8
$x^5P_3^\circ$	41, 043. 4		$z^5F_3^\circ$	30, 965. 2	141. 0
$x^5P_2^\circ$	40, 982. 7	60. 7	$z^5F_2^\circ$	30, 858. 5	106. 7
$x^5P_1^\circ$	40, 930. 2	52. 5	$z^5F_1^\circ$	30, 787. 1	71. 4
$w^5P_3^\circ$	44, 259. 5		$y^5F_5^\circ$	41, 393. 4	
$w^5P_2^\circ$	44, 187. 0	72. 5	$y^5F_4^\circ$	41, 224. 8	168. 6
$w^5P_1^\circ$	44, 125. 9	61. 1	$y^5F_3^\circ$	41, 086. 3	138. 5
			$y^5F_2^\circ$	40, 971. 6	114. 7
$v^5P_3^\circ$	45, 113. 1		$y^5F_1^\circ$	40, 906. 5	65. 1
$v^5P_2^\circ$	44, 875. 0	238. 1			
$v^5P_1^\circ$	44, 666. 7	208. 3	$x^5F_5^\circ$	45, 305. 8	
			$x^5F_4^\circ$	45, 285. 8	20. 0
$u^5P_3^\circ$	46, 878. 5		$x^5F_3^\circ$	45, 255. 3	30. 5
$u^5P_2^\circ$	46, 967. 6	−89. 1	$x^5F_2^\circ$	45, 224. 9	30. 4
$u^5P_1^\circ$	47, 021. 9	−54. 3	$x^5F_1^\circ$	45, 201. 5	23. 4

TABLE 1.—*Terms of Cr I*—Continued

Term	ν	$\Delta\nu$	Term	ν	$\Delta\nu$
$w^5F_5^\circ$	46, 704. 9		$y^5G_6^\circ$	44, 745. 9	
		−15. 3			154. 8
$w^5F_4^\circ$	46, 720. 2		$y^5G_5^\circ$	44, 591. 1	
		+32. 1			56. 7
$w^5F_3^\circ$	46, 688. 1		$y^5G_4^\circ$	44, 534. 4	
		+10. 8			161. 1
$w^5F_2^\circ$	46, 677. 3		$y^5G_3^\circ$	44, 373. 3	
		−1. 1			73. 4
$w^5F_1^\circ$	46, 678. 4		$y^5G_2^\circ$	44, 299. 9	
$v^5F_5^\circ$	47, 644. 0		$x^5G_6^\circ$	47, 222. 1	
		4. 9			−6. 5
$v^5F_4^\circ$	47, 639. 1		$x^5G_5^\circ$	47, 228. 6	
		3. 6			38. 6
$v^5F_3^\circ$	47, 635. 5		$x^5G_4^\circ$	47, 190. 0	
		4. 6			64. 2
$v^5F_2^\circ$	47, 630. 9		$x^5G_3^\circ$	47, 125. 8	
		1. 8			78. 3
$v^5F_1^\circ$	47, 629. 1		$x^5G_2^\circ$	47, 047. 5	
$u^5F_5^\circ$	47, 985. 5		$w^5G_6^\circ$	49, 635. 0	
		−28. 8			17. 6
$u^5F_4^\circ$	48, 014. 3		$w^5G_5^\circ$	49, 617. 4	
		+39. 9			44. 4
$u^5F_3^\circ$	47, 974. 4		$w^5G_4^\circ$	49, 573. 0	
		56. 6			53. 2
$u^5F_2^\circ$	47, 917. 8		$w^5G_3^\circ$	49, 519. 8	
		40. 4			53. 0
$u^5F_1^\circ$	47, 877. 4		$w^5G_2^\circ$	49, 466. 8	
$t^5F_5^\circ$	50, 253. 1		$z^5H_7^\circ$	45, 741. 2	
		42. 3			34. 1
$t^5F_4^\circ$	50, 210. 8		$z^5H_6^\circ$	45, 707. 1	
		108. 5			44. 0
$t^5F_3^\circ$	50, 102. 3		$z^5H_5^\circ$	45, 663. 1	
		44. 8			48. 3
$t^5F_2^\circ$	50, 057. 5		$z^5H_4^\circ$	45, 614. 8	
		38. 6			48. 9
$t^5F_1^\circ$	50, 018. 9		$z^5H_3^\circ$	45, 565. 9	
$s^5F_5^\circ$	53, 172. 1		$^3P_2^\circ$	34, 190. 7	
		54. 8			293. 4
$s^5F_4^\circ$	53, 117. 3		$^3P_1^\circ$	33, 897. 3	
		47. 6			134. 7
$s^5F_3^\circ$	53, 069. 7		$^3P_0^\circ$	33, 762. 6	
		32. 9			
$s^5F_2^\circ$	53, 036. 8		$^3D_3^\circ$	38, 911. 4	
		25. 2			180. 7
$s^5F_1^\circ$	53, 011. 6		$^3D_2^\circ$	38, 730. 7	
					133. 6
$r^5F_5^\circ$	54, 537. 9		$^3D_1^\circ$	38, 597. 1	
		111. 2			
$r^5F_4^\circ$	54, 426. 7		$^3D_3^\circ$	46, 174. 2	
		96. 7			65. 2
$r^5F_3^\circ$	54, 330. 0		$^3D_2^\circ$	46, 109. 0	
		76. 1			31. 9
$r^5F_2^\circ$	54, 253. 9		$^3D_1^\circ$	46, 077. 1	
		54. 0			
$r^5F_1^\circ$	54, 199. 9				
$z^5G_6^\circ$	42, 605. 5				
		16. 5			
$z^5G_5^\circ$	42, 589. 0				
		24. 2			
$z^5G_4^\circ$	42, 564. 8				
		26. 0			
$z^5G_3^\circ$	42, 538. 8				
		23. 4			
$z^5G_2^\circ$	42, 515. 4				

TABLE 2.—*Terms of Cr II*

Term	ν	$\Delta\nu$	Term	ν	$\Delta\nu$
$a^6S_{2½}$	0. 0		$a^4D_{3½}$	20, 025. 5	
					226. 0
			$a^4D_{2½}$	19, 799. 5	
$a^6D_{4½}$	12, 498. 3				166. 6
		192. 6	$a^4D_{1½}$	19, 632. 9	
$a^6D_{3½}$	12, 305. 7				103. 0
		156. 0	$a^4D_{0½}$	19, 529. 9	
$a^6D_{2½}$	12, 149. 7				
		115. 4			
$a^6D_{1½}$	12, 034. 3		$b^4D_{3½}$	25, 035. 4	
		70. 8			−13. 0
$a^6D_{0½}$	11, 963. 5		$b^4D_{2½}$	25, 048. 4	
					+3. 9
			$b^4D_{1½}$	25, 044. 5	
					+7. 2
$a^4P_{2½}$	30, 866. 1		$b^4D_{0½}$	25, 037. 3	
		557. 0			
$a^4P_{1½}$	30, 309. 1				
		355. 3			
$a^4P_{0½}$	29, 953. 8				

TABLE 2.—*Terms of Cr II*—Continued

Term	ν	$\Delta\nu$	Term	ν	$\Delta\nu$
$a^4F_{4½}$	31, 221. 1		$z^4P_{2½}°$	49, 353. 3	
		50. 8			345. 7
$a^4F_{3½}$	31, 170. 3		$z^4P_{1½}°$	49, 007. 6	
		51. 2			256. 7
$a^4F_{2½}$	31, 119. 1		$z^4P_{0½}°$	48, 750. 9	
		34. 5			
$a^4F_{1½}$	31, 084. 6		$y^4P_{2½}°$	49, 707. 9	
					141. 7
$b^4F_{4½}$	32, 855. 8		$y^4P_{1½}°$	49, 566. 2	
		17. 3			71. 8
$b^4F_{3½}$	32, 838. 5		$y^4P_{0½}°$	49, 494. 4	
		−18. 2			
$b^4F_{2½}$	32, 856. 7		$z^4D_{3½}°$	54, 786. 1	
		10. 2			158. 8
$b^4F_{1½}$	32, 846. 5		$z^4D_{2½}°$	54, 627. 3	
					126. 1
$a^4G_{5½}$	20, 514. 2		$z^4D_{1½}°$	54, 501. 2	
		−6. 9			81. 6
$a^4G_{4½}$	20, 521. 1		$z^4D_{0½}°$	54, 419. 6	
		+1. 4			
$a^4G_{3½}$	20, 519. 7		$y^4D_{3½}°$	64, 926. 2	
		+5. 5			475. 9
$a^4G_{2½}$	20, 514. 2		$y^4D_{2½}°$	64, 450. 3	
					386. 9
$b^4G_{5½}$	33, 695. 7		$y^4D_{1½}°$	64, 063. 4	
		75. 3			260. 1
$b^4G_{4½}$	33, 620. 4		$y^4D_{0½}°$	63, 803. 3	
		97. 7			
$b^4G_{3½}$	33, 522. 7		$z^4F_{4½}°$	51, 944. 5	
		103. 1			154. 0
$b^4G_{2½}$	33, 419. 6		$z^4F_{3½}°$	51, 790. 5	
					119. 4
$a^4H_{6½}$	30, 393. 4		$z^4F_{2½}°$	51, 671. 1	
		93. 1			85. 1
$a^4H_{5½}$	30, 300. 3		$z^4F_{1½}°$	51, 586. 0	
		79. 2			
$a^4H_{4½}$	30, 221. 1		$z^4G_{5½}°$	?	?
		61. 6			
$a^4H_{3½}$	30, 159. 5		$z^4G_{4½}°$	65, 385. 6	
					127. 1
$a^2P_{1½}$	17, 593. 3		$z^4G_{3½}°$	65, 258. 5	
		696. 7			100. 5
$a^2P_{0½}$	16, 896. 6		$z^4G_{2½}°$	65, 158. 0	
$a^2D_{2½}$	21, 824. 4		$z^4H_{6½}°$	64, 032. 1	
		−1. 6			181. 7
$a^2D_{1½}$	21, 826. 0		$z^4H_{5½}°$	63, 850. 4	
					142. 2
$z^6P_{3½}°$	48, 633. 9		$z^4H_{4½}°$	63, 708. 2	
		140. 9			104. 8
$z^6P_{2½}°$	48, 493. 0		$z^4H_{3½}°$	63, 603. 4	
		92. 2			
$z^6P_{1½}°$	48, 400. 8		$y^4H_{6½}°$	69, 389. 5	
					218. 0
$z^6D_{4½}°$	49, 840. 1		$y^4H_{5½}°$	69, 171. 5	
		192. 6			177. 9
$z^6D_{3½}°$	49, 647. 5		$y^4H_{4½}°$	68, 993. 6	
		155. 7			148. 3
$z^6D_{2½}°$	49, 491. 8		$y^4H_{3½}°$	68, 845. 3	
$z^6D_{1½}°$	?				
$z^6D_{0½}°$	?		$^2S_{0½}°$	47, 266. 7	
			$^2P_{1½}°$	49, 307. 9	
$z^6F_{5½}°$	47, 753. 4				198. 7
		286. 9	$^2P_{0½}°$	49, 109. 2	
$z^6F_{4½}°$	47, 466. 5				
		237. 5			
$z^6F_{3½}°$	47, 229. 0		$^2P_{1½}°$	57, 974. 0	
		186. 9			3. 7
$z^6F_{2½}°$	47, 042. 1		$^2P_{0½}°$	57, 970. 3	
		135. 2			
$z^6F_{1½}°$	46, 906. 9				
		81. 7			
$z^6F_{0½}°$	46, 825. 2				

WASHINGTON, July 18, 1930.